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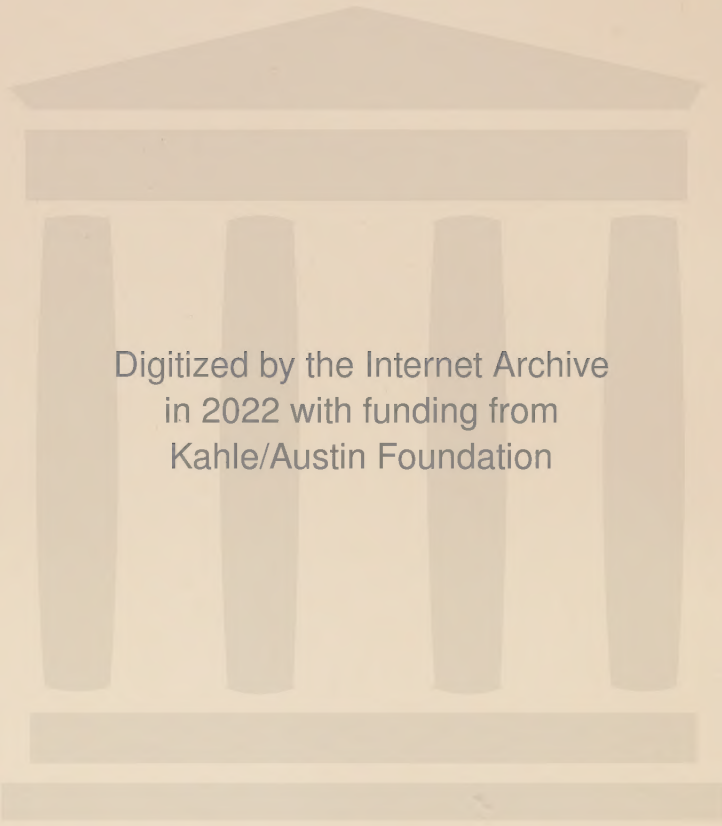
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THE LABORATORY
INVESTIGATION OF ORES



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THE LABORATORY INVESTIGATION OF ORES

A SYMPOSIUM

EDITED BY

ERNEST E. FAIRBANKS

*Department of Geology, Buffalo Museum of Science, Buffalo, New York.
Formerly Mineralogist, Rare and Precious Metals Experiment
Station, U. S. Bureau of Mines, Department of
Commerce, Reno, Nevada.*




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LIST OF CONTRIBUTORS

- N. L. BOWEN, Petrologist, Geophysical Laboratory, Carnegie Institution of Washington, D. C. Geologic Thermometry.
- R. J. COLONY, Assistant Professor of Geology, Columbia University, New York. Ore Mineral Sequence.
- WHEELER P. DAVEY, Professor of Physical Chemistry, Pennsylvania State College. Formerly Research Physicist, Research Laboratory, General Electric Company, Schenectady, New York. Crystal Analysis by Means of X-rays.
- ERNEST E. FAIRBANKS, Department of Geology, Buffalo Museum of Science, Buffalo, New York. Formerly Mineralogist, Rare and Precious Metals Experiment Station, U. S. Bureau of Mines, Department of Commerce, Reno, Nevada. Microscopes, Their Construction and Use; Dielectric Methods; Zonal Distribution.
- F. N. GUILD, Professor of Optical Mineralogy, University of Arizona, Tucson, Arizona. The Enrichment of Silver Ores.
- ALFRED C. LANE, Pearson Professor of Geology, Tufts College, Medford, Massachusetts. Genetic Significance of Grain.
- WALDEMAR LINDGREN, William Barton Rogers Professor of Economic Geology, Massachusetts Institute of Technology, Cambridge, Massachusetts. Historical Review of the Study of Polished Sections of Opaque Minerals.
- R. P. LOVELAND, Research Laboratory, Eastman Kodak Company, Rochester, New York. Practical Photomicrography.
- W. H. NEWHOUSE, Instructor in Geology, Massachusetts Institute of Technology, Cambridge, Massachusetts. The Microscopic Criteria of Replacement in the Opaque Ore Minerals.
- G. M. SCHWARTZ, Assistant Professor of Geology and Mineralogy, University of Minnesota, Minneapolis, Minnesota. Ore-Dressing Microscopy.
- G. A. THIEL, Assistant Professor of Geology and Mineralogy, University of Minnesota, Minneapolis, Minnesota. The Textural Relationships of the Opaque Manganese Minerals.
- A. P. H. TRIVELLI, Research Laboratory, Eastman Kodak Company, Rochester, New York. Practical Photomicrography.

PREFACE

A vast amount of work on ore minerals has been completed since Campbell first applied the methods of the metallographer to their study. It is fitting, therefore, to present some of the results of this study as well as new developments of methods. Thus it is possible not only to take account of stock but to point out future directions for investigation. If this publication succeeds in aiding the future advancement of the subject the editor and contributors will feel well repaid for their efforts.

In the selection of subject matter for this symposium, omission has been made purposely of certain subjects of great importance to the study of ores which have already been presented elsewhere in an excellent manner. On the other hand subjects have been included which, in the editor's opinion, appeared to require more thorough treatment.

In a symposium it is usually natural that conflicting statements make their appearance. It is conventional for an editor to note the fact without attempting to prevent their appearance; more than one point of view obviously being of greater value. Such conflicting statements sometimes stimulate further research. An interesting example is presented by the interpretation of mutual boundaries which Prof. Colony illustrates in Fig. 1, page 135. Dr. Newhouse illustrates (Fig. 8, p. 161) a case of mutual boundaries also which was formed artificially yielding a conclusion contrary to that generally accepted.

Chapter IX, entitled, "The Textural Relationships of the Opaque Manganese Minerals" has been included as an example of the information to be obtained by the application of data such as are presented in other chapters of the book. The original plan was to include a description of as many groups of metallic minerals as possible but circumstances prevented its fulfillment. The reader, as well as the editor, will appreciate the inclusion of this chapter even though the departure from the original plan excludes descriptions of other important mineral groups.

The editor is indebted to the contributors who, through deep interest in this relatively new science, the study of ores by means of the microscope, though having little time for this purpose, were willing to prepare the chapters making the book possible.

ERNEST E. FAIRBANKS.

BUFFALO, N. Y.,
September, 1928.

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LABORATORY INVESTIGATION OF ORES

CHAPTER I

HISTORICAL REVIEW OF THE STUDY OF POLISHED SECTIONS OF OPAQUE MINERALS

BY WALDEMAR LINDGREN

It is fascinating to watch the development of a new idea, its gradual growth, the growth of new viewpoints concerning it, and its final definite position in the world of science. The only difficulty is that the importance of a new idea is rarely recognized at once; little attention may be paid at first; its originator may even at first be thought somewhat of a crank. The truth is that the retrospect is far more easy than the prognostication. In a marked degree this applies to the study of polished sections of opaque minerals, which is properly a branch of mineralogy, but which finds its chief application in the examination of ores.

For many years, mineralogists have known that the structures of ore minerals are best seen on polished surfaces, and every large collection had its share of such material. But, somehow, the application of the microscope to such material, simple as it proved, was slow in coming. We were used to thin sections, which, of course, have the advantage of enabling us to identify the non-metallic minerals by optical means. But the cover-glass and the confusion arising from the fact that we were looking through an appreciable thickness of material made difficult the identification and the relations.

In polished sections made by proper methods, one plane only is exposed, and the interrelations of the minerals are shown in startling precision. The substances can be examined by micro-chemical methods and by etching; even minerals occurring in small volume can be isolated and tested.

Quite naturally, the new method was found by the way of metallography, which comprises the study of polished sections of metals. We owe the start of metallography to H. C. Sorby, who, after having initiated the preparation of transparent rock sections, late in 1864 began to study such polished sections of metals and metallurgical products by aid of the microscope. This new idea was by no means followed up promptly. It was not until 1878 that Martens published his paper on "The Microscopical Examination of Iron." Even from then, the progress was not rapid, but the work of Bayles, Dollick, Garrison, Osmond and Werth, Wedding, Howe, Roberts-Austin, Le Chatelier, and many others followed from the date mentioned to about 1900. The work was at first purely descriptive, but the technique was slowly developed; and soon thereafter, the relations and combinations of metals in alloys was placed on a stable thermodynamic base by the fundamental work of Roozeboom, Van't Hoff, and Tamman.

At an early date, metallic alloys occurring in nature were also examined; particularly I refer to Cohen's work on meteorites, about 1894.

H. Baumhauer,¹ in 1885, examined polished specimens of bornite and chalcocite with the microscope, and E. Hussak² polished and etched titaniferous magnetite.

It is to the great credit of Dr. W. Campbell of Columbia University, the well-known investigator of metallography, that he definitely initiated the application of the method to metallic ores, in his paper on "The Microscopic Examination of Opaque Minerals."³

This was immediately followed by an article by Campbell and Knight on the cobalt silver ores and, later, by similar investigations on the Sudbury, Ontario, nickel ores. The method of preparing sections was described, the minerals identified, etching methods suggested, and the succession of deposition of the individual minerals determined.

One would think that economic geologists would have acclaimed with enthusiasm such a valuable addition to their tools of research, but such is the inertia even of scientific men that several years elapsed with but occasional contributions, and those

¹ BAUMHAUER, H., *Krys.*, Vol. X, 1885, p. 447.

² HUSSAK, E., *Neues Jahrb. Mineral Geol. u. Pal.*

³ CAMPBELL, W., *Econ. Geol.*, Vol. I, pp. 751-766, 1906.

mainly from students of Columbia University under the direction of Dr. Campbell. We note among those, F. C. Lincoln's paper on the "Promontario Silver Mine, Mexico,"¹ and an article by J. F. Simpson on the "Copper Ores of Butte, Montana."² From 1911, a wider interest may be discovered. In that year came F. B. Laney's notable paper on the relations of bornite and chalcocite at Virgilina, Virginia.³ In 1913, appeared E. S. Bastin's study of metasomatism in downward sulphide enrichment, the first indication of any activity in this direction by the U. S. Geological Survey, and in the same year appeared the important paper by L. C. Graton and J. Murdoch⁴ on the sulphide ores of copper.

Looking back on these early years, I am somewhat at a loss to account for the slow acceptance of such a promising new line of examination. I feel not entirely blameless, for during that time I was actively engaged in this federal survey on metaliferous deposits. As a matter of fact, I believe I made my first polished sections of chalcocite ores in 1910 or 1912 in the Massachusetts Institute of Technology. Graton and Murdoch began their investigation in 1911.

From 1913, the progress of this kind of investigation began to be much more rapid, and individual papers cannot be enumerated. The work, however, centered in comparatively few places in the United States; as yet it had not spread to Europe. It was carried on at Columbia University, under Campbell; in the U. S. Geological Survey, by Bastin; at the University of Arizona, under Guild; in Harvard University, under Graton; at Stanford University, under Tolman and Rogers; and at the Massachusetts Institute of Technology, under Lindgren. Methods of grinding, polishing, and photography were considered; criteria of replacement were investigated, for it soon became evident that successive replacements played a most important part in metallic ores; methods of etching were standardized. At last, in 1916, based on work at Harvard University, appeared Murdoch's book on "Microscopical Determination of Opaque Minerals." For the first time, exact tables were avail-

¹ LINCOLN, F. C., *Trans. Am. Inst. Mining Met. Eng.*, Vol. XXXVIII, 1907.

² SIMPSON, J. F., *Econ. Geol.*, Vol. III, 1908.

³ LANEY, F. B., *Econ. Geol.*, Vol. VII, p. 75, 1912.

⁴ GRATON, L. C., and J. MURDOCH, *Trans. Am. Inst. Mining Eng.*, Vol. XLV, 1914, and *Econ. Geol.*, Vol. VIII, 1913.

able for the mineralogical diagnosis, and they proved of inestimable value.

The question of a name for the new method of work came up. Murdoch and Graton preferred *mineralography*, which obviously includes a wider field than that actually covered. Later, W. L. Whitehead suggested *mineragraphy*, from the later "minera" ore. It seems to me that this is probably the best name proposed, though, personally, I find myself often circumventing it by using the expression *metallographic methods*. Still later, H. Schneiderhöhn proposed *chalcography*, a name already preempted for other purposes in this country and for that reason hardly to be accepted.

In 1920, Davy and Farnham brought out another set of determinative tables entitled "Microscopic Examination of the Ore Minerals," based on work at Harvard and at the Massachusetts Institute of Technology. It was found that the determination of slight differences of color, which in Murdoch's scheme is an important diagnostic factor, was difficult for many students whose color sense was not always sharp. This book is now in general use. It is an excellent guide to identification, when intelligently used. But, as many students have ascertained to their sorrow, it is by no means foolproof.

The first period now drew to an end. Perhaps the most prominent production of this time is Tolman and Rogers' book on the "Study of the Magmatic Sulphide Ores" (1916), with its excellent description and unequaled photographs.

By this time, the study of mineragraphy had spread to Europe. Really, its introduction to that continent was effected by Schneiderhöhn, who, while interned at Tsumeb, during the war, became interested in these problems. He published several papers and, in 1922, a book entitled "*Anleitung zur Mikroskopischen Untersuchung von Erzen*," which, though mainly diagnostic, contains a number of new and important viewpoints. The merit of having introduced a practical method of determining the double refraction of opaque minerals by reflected light belongs chiefly to him, though credit must also be given to his predecessors, J. Königsberger and Fred Wright.

In 1925, we find another European book on the subject. I refer to "Mineragraphy and Ore Deposition," by R. W. van der Veen, whose early death has caused a great loss to science. This, too, is rich in diagnostic detail and fine photographs, but

perhaps its chief merit is the introduction of physical chemistry into this branch of study. Not that that had been neglected entirely before; Schneiderhöhn had published many important papers on the subject, most important of which, perhaps, is the application of *unmixing* to the products of ore deposition.

The diagnostic and purely descriptive era has passed in part. What now looms up before us is the interpretation of the results by the methods of thermodynamics. The problem which occupied the earlier authors besides the diagnosis was the succession and replacement of minerals. It is now up to us to explain the reason why, and the only way to do this is through physical chemistry. Why do we find in almost all ores of magmatic affiliations a definite succession, always beginning with pyrite and arsenopyrite and generally followed by sphalerite? As in metallography, the explanation must be based on Roozeboom's, Tamman's, and Van't Hoff's thermodynamics, but the conditions are more complicated. Instead of a simple solidification from a known melt, we have to explain deposition by generally fluid solutions of more or less unknown composition and most complex phenomena of replacement. Fairbanks, among others, has brought forward the close relationship of many of the problems of metallic alloys with those of metallic ores.

To many of our European *confrères*, replacement is, it seems to me, still more or less of a sealed book. At least, they scarcely recognize its extreme importance. But previously to this, comes the recognition of the criteria of replacement, and it must be confessed that all of us do not always agree on the details of these. The tendency of one school is to emphasize contemporaneous deposition of many minerals and to establish criteria for this by *mutual boundaries*, or curved boundaries between metals, without apparent evidence one way or the other; and also to hold that the so-called *graphic intergrowths* of ore minerals prove contemporaneous deposition. Personally, I confess that I lean rather strongly the other way. In most ore, I find good evidence of a definite succession. The mutual boundaries prove to me but little. And I see in the graphic intergrowth simply the replacement of one mineral by another. This is scarcely the place, however, to thresh out this question.

Still another problem on which the study of polished sections may throw much light relates to the deposition of colloid mineral and colloid replacement.

It is, perhaps, pardonable to point with some satisfaction to the fact that mineragraphy had its origin in our country and that we have a good-sized company of eager and able workers who will, in time, advance the study far beyond the present limits. Among the present most active workers may be mentioned Laney, Bastin, Short, Gilbert, Schwartz, Broderick, and Grout. In connection with this, I may call attention to a regrettable fact: Many and very excellent papers have been published which are theses for the Masters' or Doctors' degrees, but, in most cases these authors are never heard from again, apparently having lost their interest in mineragraphy as soon as they obtained the desired title.

With the diagnosis, chemistry, and particularly microchemistry must go hand in hand. For the explanation of the structures and the succession, physical chemistry must be relied upon, aided by experimental work at higher temperatures and pressures. We have an unequaled tool in our hands to trace in minutest details the intricate structures and relations. It is up to us to use this tool in an intelligent manner.

I do not say that the descriptive phase of the science is past, for we have thousands of occurrences which have not yet been described, and the ores of some metals have scarcely been touched. Needless to say, the investigator must be supported by field evidence or *vice versa*. Either one without the other is unsatisfactory.

I have referred to certain practical applications in which mineragraphy is of the greatest assistance. Foremost among these is the examination of ores or of crushed mill products with a view to determining the best methods of concentration. Our Bureau of Mines has made a good beginning in the important field, and European authors, such as Schneiderhöhn, have also discussed this subject.

All in all, it can be said that mineragraphy is in a very healthy state of development and that a great deal can be expected of it in the future.

CHAPTER II

MICROSCOPES, THEIR CONSTRUCTION AND USE

BY ERNEST E. FAIRBANKS

Microscopes.—In the laboratory investigation of ores, a petrographic microscope is indispensable. Most ore minerals are opaque, therefore transmitted light is excluded in their study; however, the most important method of identifying opaque minerals is probably by means of microchemical reactions which convert the opaque substances into transparent microcrystals, permitting the study by transmitted light with the petrographic microscope. This microscope can also be easily fitted with a vertical illuminator for study of the opaques directly. One other method of promise, at least, involving the study of opaques by reflected polarized light, requires the use of the finest type of petrographic microscope available.

In order to prevent repetition, the following discussion will be limited to the petrographic microscope. The reflecting microscope is of much simpler construction, and all essential features are covered in the description of the petrographic microscope.

Wright¹ gives the following requirements which are usually considered important in the mechanical construction of the petrographic microscope:

1. Firm, rigid stand for the support of the optical system.
2. Optical system centered; optic axis of the system to pass through the center of the rotation of the stage.
3. Simple device for centering objectives. Centering screws parallel, not diagonal, to cross-hairs of ocular in order to use field coordinates as guides. To center the stage instead of the objective is wrong in principle, as it displaces the one point to which the optical system is tied.
4. Easy passage from parallel to convergent polarized light.
5. Easy passage from low to high powers.

¹ WRIGHT, F. E., "The Methods of Petrographic-microscopic Research," *Carnegie Inst. Pub.*, Vol. CLVIII, pp. 12-13, 1911.

6. Bertrand lens centered and adjusted to proper focus.
7. Properly constructed coarse and fine adjustment. Fine-adjustment screw to record intervals of 0.001 millimeter and to be free from lost motion.
8. Satisfactory arrangement for raising and lowering substage condenser.
9. Accurately constructed mechanical stage on which lateral movements of 0.01 millimeter can be measured directly.
10. Degree circle of stage to be accurately divided and provided with vernier to read to 5 minutes at least.
11. Ocular, the upper Nicol carriage, the Bertrand lens support, all moving parts to fit accurately so that on insertion they invariably return to exactly the same point.

With regard to centering objectives (3), it is not essential that the centering screws be parallel to the cross-hairs, since the ocular can be turned to the diagonal position. The important point is to insure that the centering screws be placed on the objective mounting rather than in any other position.

Unquestionably one of the most important mechanical devices of the microscope stand, if not the single most important feature, is the fine adjustment (micrometer screw). The slightest error and faulty movement in its mechanism is correspondingly magnified with the magnifications obtained with the microscope. Great care and the highest type of precision workmanship are required in the fitting of the individual sliding parts of the micrometer device and its bearing surfaces. These surfaces are required to be adjusted with minute accuracy, without the least bit of lateral displacement being noticeable; otherwise a slight lateral play of the microscopic image would be produced. The sliding motion must also be accomplished in such a perfect manner that the slightest turn of the micrometer screw will compel the microscope tube, with the objective, to follow without vertical lost motion.

The microscope stands which have been constructed during the last decades provide a micrometer movement based either on prismatic surfaces or on dovetailed sliding bearings. In these constructions, the surfaces which glide upon each other must consist of different alloys, so that one surface represents a degree of hardness different from the other surface upon which it glides. Furthermore, an appropriately selected lubricant had to be utilized to furnish these gliding surfaces with the desired

smoothness of movement, since only the correct constituency of the lubricant would give a correct functioning of the micrometer movement. It is interesting to note that these early types of movements would not function under a too-great temperature change; the lubricant congealed in cold climates and became too soft in hot climates.

Difficulties which are likely to impair the satisfactory functioning of a micrometer movement also result from the weight of the microscope tube, especially in the case of the binocular tubes now used to a great extent. The tubes of polarizing microscopes, binocular stereo attachments, and photomicrographic camera attachments also create undue weight upon the micrometer screw. The unbalanced weight impairs the proper functioning of the micrometer screw; consequently, the necessity of improving micrometer movements became important.

The best type of fine adjustment yet devised is a micrometer threaded construction in which the minimum number of threads completely engaged through 360° is 34. It also transmits the motion as a direct upward thrust of the body tube. If a lateral displacement of the image should appear when using this fine adjustment, the light from the mirror has not been properly centered. The use of a spring is a simple and efficient mechanical means of entirely eliminating the effect of any lost motion which may develop.

Elementary mechanical laws indicate that considerable weight, such as the weight of a binocular body, acting against certain micrometer fine-adjustment devices will change the focus. It is advisable to test the fine adjustment by removing the hand from the fine-adjustment knob after focusing upon a very fine structure and observing if this focus is maintained.

In choosing a binocular body, attention should be given to the following important features:

1. Intensity of binocular prism body. If the construction involves a greater number of prisms or longer ones than another make, it is possible that the total intensity will be lowered appreciably in the body containing the most glass. Thus, there is a difference in intensity amounting to 10 per cent between two of the finest makes.

2. Evenness of brightness.

3. Dustproof construction.

4. Adjustment of the interpupillary distance.

5. It is essential to have a special focusing adjustment on the left tube, to compensate for differences in the eyes of the observer. This feature is sometimes missing.

In the case of the petrographic microscope, the binocular body is attached by removing the ocular of the monocular tube. It may be possible to construct a petrographic microscope less unwieldy with binocular vision which can be used for obtaining interference figures.

In using an objective of numerical aperture (N.A.) greater than 1.0, an immersion condenser of N.A. 1.40 should be screwed into the swing-out mounting in place of the condenser of N.A. 1.0. Although the necessity of employing a different condenser in high N.A. work is pointed out in the microscope catalogues, it is a common procedure to employ the component of low N.A. in this work. The N.A. of the immersion condenser is engraved on the mounting. To obtain a N.A. of 1.40, the object slide must be kept within narrow limits. A thickness of from 0.9 to 1 millimeter being the limit although a new construction will appear soon in which this latitude will be slightly increased.

The modern petrographic microscope made by the most reliable manufacturers leaves the factory with the mechanical and optical adjustments carefully checked by experts. The petrographic microscope is a much more delicate instrument than most of the non-polarizing instruments, as a result of the necessity of making extremely fine measurements and the profound effect upon conoscopic observations of an improperly adjusted instrument. The vibrations to which it is subjected incidental to transportation, including rough handling, as well as the changes which gradually take place in all metals with relief of stress, make it essential that special provision for adjustment by the ultimate purchaser be provided.

Before a new or unfamiliar instrument is used, tests should be made for the following:

1. Accurately crossed Nicols. The principal planes of the nicols when crossed must be exactly 90 degrees apart.

2. The cross-hairs of the ocular must coincide with the principal planes of the Nicols.

3. Optical system accurately centered.

4. The coincidence of the optical axis of each objective, when attached to microscope, with the optical axis of the other parts of the optical system.

To test the crossed position of Nicols: Remove all lenses, cross the Nicols, and point microscope directly at the sun. A rotation of less than 10 minutes is easily detected if the Wright bi-quartz wedge-plate is employed on the stage. As the eye is more sensitive to a slight change in color than to slight differences in degree of intensity, it is advisable to employ the Wright accessory.

To align the cross-hairs of the ocular with the principal planes of the Nicols: Employ a thin section containing a mineral with excellent cleavage and parallel extinction. Determine the position of extinction accurately by means of bi-quartz plate and place mineral in position of zero extinction. The cross-hairs are brought parallel to the cleavage lines.

Objectives are easily centered by the screws on the objective mount. With a micrometer ocular, the rotation of a fine grain occurring in a thin section can be made to cut all four lines of cross-hairs encountered upon rotation an equal distance; or, in other words, the rotation makes a perfect circle.

When using iris diaphragm, the aperture should not be made less than 0.5 millimeters in diameter, otherwise diffraction phenomena may be encountered.

In order to avoid all suspicion of optical properties obtained from a mineral occurring in thin section, it should be studied in isolated grains in order that it alone will be responsible for the properties observed.

It is a difficult matter to attempt a discussion of future improvements of the petrographic microscope. Nevertheless, there appears to be a tendency toward combining the features of the reflecting microscope with those of the polarizing microscope. Even at the present time, it is possible satisfactorily to arrange the petrographic microscope for the study of opaques. The important features which should be embodied in the arrangement for work with opaques follow:

1. *Vertical*, or opaque illuminator.
2. Short-mounted objectives. Such objectives are corrected for use without cover-glass, and their use insures the proper passage of light through the prism of illuminator.¹

¹ Short mounts reduce the tendency of the prism or the aperture stop to act as a field stop and cause uneven illumination. According to WRIGHTON, "The Photomicrography of Metals," *Jour. Roy. Micro. Soc.*, Vol. XLVII, p. 114, June, 1927, there is no necessity for short mounting when glass plate is used in the illuminator and objective is fully illuminated. The standard high-power immersion objective in its longer mount, well blackened inside, may even be preferable in this case.

3. Draw-tube. The short-mounted objectives used with a vertical illuminator give proper tube length without necessity of employing draw-tube. If other objectives are used tube length would not be correct. The presence of a draw-tube covers all cases.

4. Rack and pinion for raising and lowering stage of microscope, and locking device for locking it at any desired height.

This type of stage, permitting vertical adjustment, is undoubtedly one of the features which will be included on the best future petrographic stands. A *built-in* mechanical stage, with stage of larger diameter than the ordinary types, is often furnished at the present time on special order. This should become standard equipment on at least one model.

All of the above features can be added to a petrographic microscope at slight additional cost.

Now that binocular vision has been perfected, provision for a binocular body as an essential part of the instrument, rather than as an attachment, may be a future possibility.

Illuminators for the study of opaques are constantly being improved (see mention of type devised by Mr. Jewell in chapter on Practical Photomicrography), and undoubtedly the future will see additional improvements along this line.

An electromagnetic arrangement has been devised independently by R. G. Guthrie, E. E. Fairbanks, and, according to information recently received, others, for maintaining accurate focusing for high-power photomicrography.

Eye Strain.—According to Dr. Exton,¹ “. . . no technician who began with tested emmetropic² eyes has been encountered by us who managed to continue routine microscopy longer than two years without finding it necessary to be fitted with glasses.” If the above statement is that of a general fact, microscopists should give the subject of eye strain more attention than they have given it in the past. It has, therefore, been considered advisable to present very briefly a few remarks on eye strain and its prevention.

The microscopist who develops eye strain is usually found to have some slight muscular deficiency or error of refraction.

¹ EXTON, WILLIAM G., “The Euscope as an Aid to Microscopy,” *Jour. Am. Med. Assoc.*, Vol. LXXXII, No. 23, p. 1838, 1924. Quoted by WALDSCHMIDT, W. A., in *Colo. School Mines*.

² Having normal vision.

Muscular fatigue of the eye has probably been experienced by everyone who has made use of the microscope to an appreciable extent. The majority engaged in microscopic work employ a monocular microscope and become accustomed to the use of one eye. After several hours of observation, the eye which has not been used will be tired, not the eye which has been used. The unemployed eye, in seeking a suitable point to focus on, causes the muscle known as the *ciliary muscle*, to change the form of the crystalline lens. This process, whereby the normal eye is enabled to focus on the retina in succession sharp images of objects at different distances, is called *accommodation* and consists chiefly in a change in the convexity of the anterior surface of the crystalline lens. In the passive eye, the *suspensory ligament* holds the elastic substance of the lens flattened in front. During the act of accommodation, the ciliary muscle contracts, and this contraction is accompanied by a relaxation of the ligament of the lens. The moment this relaxation takes place, the lens is permitted to become more convex by means of its own elasticity. The continuous movement or spasm of the ciliary muscle develops fatigue and may produce a more serious disorder. Emmetropia is comparatively uncommon, occurring in not more than 1.5 to 2 per cent of properly examined eyes. Thus, a slight error of refraction may be present in eyes which for all practical purposes may be classified as normal. In the case of a street-railway curve greaser, this error of refraction may never cause trouble throughout the life of the individual. In the case of a microscopist, the nature of his exacting work tends to aggravate this refractive error, resulting in serious disorder.

A microscopist may even lose the third-dimensional effect or stereoscopic vision from continuous use of one eye to the exclusion of the other.

To prevent eye strain, the writer can only suggest the addition of a binocular attachment to the monocular microscope. A binocular attachment does not eliminate eye strain if it is constructed with parallel eye tubes since the eyes must change from the parallel position to the converging position for the purpose of making notes, to change slides or to read.

The Spencer Lens Company supplies a binocular body in which the eye pieces are inclined at 4 degrees from the normal, giving them an angle of 8 degrees to each other. They also

indicate that such convergence conforms to the position assumed by normal eyes in examining ordinary objects or in reading common print. It is a fact that many people have difficulty in blending the two images obtained with parallel tubes into one picture. In a case of this kind, naturally, the converging tubes are essential.

Objectives.—The apochromatic objectives introduced by Abbe, in 1886, possess the best color correction and resolving power. The increased efficiency in optical properties is due to the use of fluorite in their construction. Fluorite has a comparatively low index of refraction ($n_D = 1.4338$) and an extremely small dispersion.

Dispersive power or relative dispersion is the ratio of the dispersion of two colors to their mean index minus one, but in place of this value it is more convenient to employ Abbe's method giving the reciprocal of this function. Thus, the reciprocal of the relative dispersion, ν , for fluorite is obtained as follows:

$$\nu = \frac{n_D - 1}{n_F - n_C} = 95.4$$

$N_F - N_C$ refers to the partial dispersion (dispersive power with respect to the visible spectrum) in the brightest part of the spectrum comprised between the Fraunhofer lines C (red) and F (blue). While the retina of the normal human eye is most sensitive to the portion of the spectrum between the C and F lines, it also shows a distinct maximum of visual effect in that region corresponding to wave lengths lying between the lines D and E, or the yellow-green region.

ν is rarely as high as 66 in any of the available optical glasses of low-refractive properties (light phosphate crown $\nu = 70$). The combination of fluorite with a much less refringent glass than the usual types of flint glasses, eliminates spherical aberration in a more efficient manner. The relative position of the spectrum color bands, as produced by a fluorite prism and with some of the glasses, is very nearly similar. It is, therefore, possible to unite at least three optically significant colors, whereas with the crown and flint pairs it is not possible to bring more than two differently colored rays to a focus.

The original amount of stress produced in the manufacture of an objective should be as low as possible, so that when the gradual relief of stress occurs, a minimum effect will result in the

objective-lens system. The minute error produced by the change in position of a lens due to relief of stress unquestionably is an important one, producing marked inaccuracies especially in the results obtained with a high-power objective of high numerical aperture. For this reason, it is worth while to mention the methods of mounting objective lenses.

An optician in Weimar, Germany, was apparently the first to devise the simplified method of mounting lenses by means of spacing rings disposed between individual lens holders of the objective-lens system. This method was at first patented by a microscope manufacturer in Germany, and more recently a United States patent has been granted on what, apparently, is a similar method, so that at the present time at least two large manufacturers of objectives employ this method of mounting objective lenses.

The older method employed individual lens holders which screwed on to the tube or mount. One other method employed the metal holder spun around the glass lens. This latter method does not yield a N.A. greater than 1.30.

Stress, of importance in the objective-lens system may occur in the cement which is used to mount the lenses in the objective tube. One manufacturer at least eliminates the stress which may develop in the cementing process.

The manner of mounting objective lenses is also important in connection with the possible production of capillary attraction, which will permit leakage of oil, in the case of oil-immersion work, into the lens system.

An objective cannot show its full efficiency unless the N.A. of the condenser used in conjunction with the objective is sufficiently high to fill completely the back of the objective with light. If the eye piece is removed from the tube of the microscope, it is possible to view the back lens of the objective and determine if it is completely filled with light.

Three simple methods of testing microscope objectives follow. The third method, while the most scientific in principle, requires expensive apparatus in its application.

The diffraction images produced by the minute structure of an object can be obtained by examination of a specimen of *Pleurosigma Angulatum*. Place the test diatom on the stage and examine with a one-twelfth oil-immersion objective, N.A. 1.25 or higher. Oil contact must be made between substage condenser

and slide—a very frequent oversight of microscopists—as well as between the objective and slide. See that the iris is partially closed, and remove eye piece. At the back lens of the objective a white central image of the iris will be seen surrounded by six diffraction spectra. The outer portion of these diffraction spectra is red, while toward the central white image a blue color will be noted. This is a very simple means of testing an objective to determine if it transmits the diffraction spectra necessary for resolution of fine detail and requires only a slide of the test diatoms.

The Abbe test plate¹ has been devised for the purpose of testing objectives for determining the thickness of the cover-glass at which the correction of the spherical aberration attains its best value. The test plate consists of groups of parallel lines ruled upon a film of silver deposited upon the back of a cover-glass. The lines are so spaced that they may be readily distinguished from one another with the lowest powers. The edges of these ruled lines are also a sensitive test object under the higher magnifications, because of the fact that the coating of silver is extremely thin. The thickness of the cover-glass is indicated by a graduated scale in which the intervals amount to 0.01 millimeter. This scale covers all thicknesses for which correction collar of objective was devised to treat.

Before using the Abbe test plate, set draw-tube of microscope at proper distance, usually indicated by a continuous line engraved around draw-tube. If a nose piece is being used, its size is deducted from the tube length ordinarily employed providing the microscope is an old model. The draw-tube of the latest constructions, fitted with a nosepiece, should be set at the position indicated by the continuous line. The condenser must be carefully centered and the light must completely fill the back of the lens of the objective. To center condenser, close diaphragm until its edge can just be seen through the back lens of the objective. Center this edge with the rim of the objective by means of centering screws on condenser mount. Use the compensating oculars (periplan of Leitz or compens of Spencer, for example) with objectives of N.A. > 0.5 and Huyghenian oculars below this value. When using central illumination, insure that there is no obliquity in the direction of light from the mirror. On using oblique illumination, insure that the light

¹ Directions for using the Abbe test plate: ZEISS, CARL, *Pamphlet* 116.

always enters at right angles to the direction of the lines on the test plate.

To test an objective of large aperture, it is focused upon various portions of the wedge in succession and the quality of the image is judged in the middle of the field of view. Any changes are noted produced while viewing alternately with direct (central) and extremely oblique light. An objective can be considered as having perfect spherical correction with respect to a thickness of cover-glass indicated by the scale on test plate (1) if the contours of the silver edge remain sharply defined at the center of the field without exhibiting hazy borders or blurred appearance with oblique light; (2) if the transition after accurate focusing from oblique illumination to direct central light does not occasion any necessity to correct the focusing adjustment in order to restore the perfect definition of the contours.

If an objective satisfies these requirements at one particular spot of the wedge, it may be stated to be free from spherical aberration at the particular cover-glass thickness indicated.

With a chromatically well-corrected achromatic objective, the edges of the silver should exhibit only narrow color fringes in the center of the field, which are composed of complementary colors of the secondary spectrum, for example, yellowish green to apple green on one side and violet to pink on the other. The primary colors are the rainbow colors, while the secondary colors are those formed by unions of these different residuals, such as purple formed by the union of red and violet. The more perfect the correction of the spherical aberration the purer will be the color appearance of these borders. When the chromatic aberration is not sufficiently corrected, other colors, such as blue and red, will make their appearance.

On the test of apochromatic objectives, the colors of the secondary spectrum should disappear in the middle of the field of view. Very narrow borders of the so-called *tertiary spectrum* are all that should remain.

Contours may appear indistinct toward the edge of the field of view, and the peripheral portions of the field may contain colored borders in the best objectives, whenever the aperture exceeds a certain value. The colors at the periphery of the field produced with an apochromatic objective of high numerical aperture and due to unequal magnification of the differently

colored images are corrected by the compensating ocular. On this ocular, the magnification of different colors is in the opposite order from that produced by the objectives—hence, *compensating*.

Objectives may be tested by a very simple method involving the use of a special type of interferometer, such as the Hilger microscope objective interferometer. By means of this instrument, spherical and chromatic aberration, coma, astigmatism, curvature of image, and distortion can be measured quantitatively.

The instrument is arranged so that a collimated beam of monochromatic light is separated into two beams at the partially silvered surface of a plane parallel glass plate. The transmitted beam passes through a converging lens under test and is reflected back from the surface of a convex mirror which is so disposed as nearly to coincide with the approximate spherical wave front of the light as it converges. This results in a plane wave front returning to the plane parallel plate. At this plate, the wave front meets the wave front of the light which has been reflected from the rear surface of the plate, has passed to a plane mirror, and has returned to the plane parallel plate. The two wave fronts thus formed meet and pass to the eye of the observer. Inasmuch as the curvature of the wave front of the transmitted beam depends upon the effect of the test lens upon this beam, any variation from the usual circular interference fringe pattern may be ascribed to the effect of the test lens. The pattern formed, according to description by F. Twyman,¹ is a contour map to a scale of $\frac{1}{2}$ wave lengths of the aberrations of wave surface occasioned by the passage of a plane wave through the test lens (Fig. 1).

Complete microscopes as well as objectives may be tested upon this principle, and with accessory attached to the interferometer, microscope stands can be tested for rigidity, and slow movements of the fine adjustments tested for accuracy. The interferometer can also be arranged for ultra-violet systems.

The subject of objectives is, of course, incomplete without reference to resolution. Depth together with good resolution has been the goal of many, regardless of its entire disregard for optical laws. For this reason, it has been considered advisable

¹ TWYMAN, F., "The Hilger Microscope Interferometer," *Jour. Optical Soc. Am.*, Vol. VII, No. 8, pp. 635-656, August, 1923.

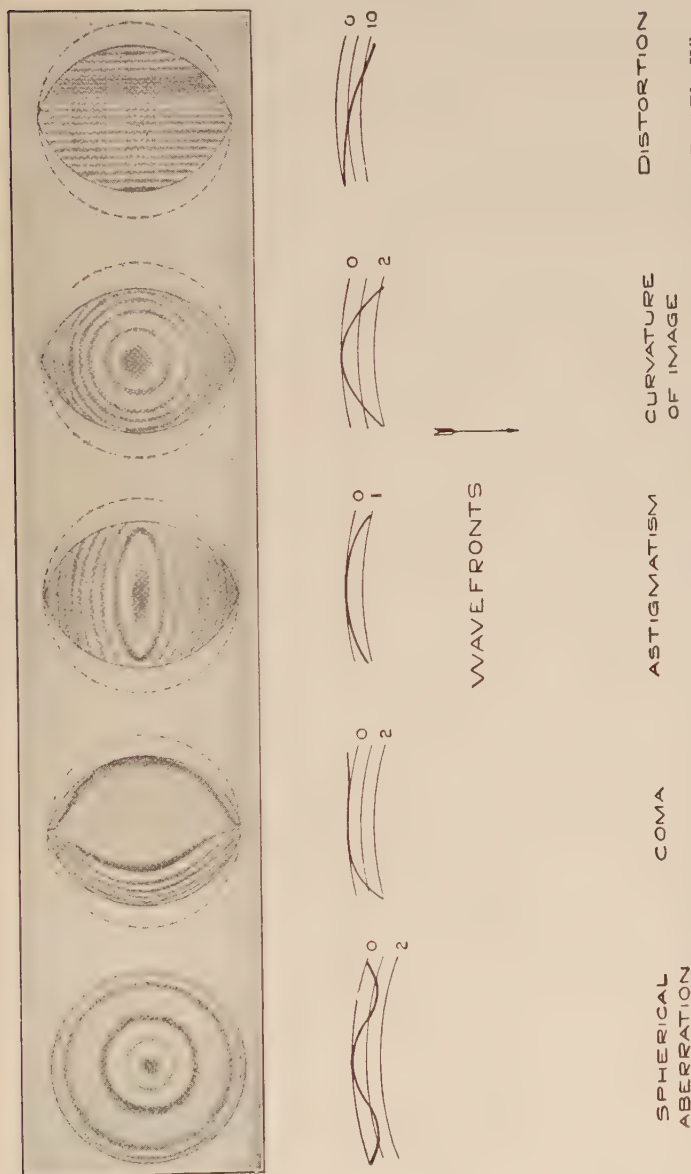


FIG. 1.—Interferograms and sections of wave fronts after single passage through lens. (From Twyman, F., "The Hülger Microscope Interferometer," *Jour. Optical Soc. Am.*, Vol. 7, No. 8, August, 1923. By permission.)

to treat the subject of resolution in greater detail than it is ordinarily treated. Dismissing the subject with the conventional formula and too-brief presentation may be partially responsible for the vast amount of time which has been wasted on attempts to combine depth and good resolution by ordinary methods.¹

While there is a definite limit to our ability of obtaining depth and resolution on the basis of optical laws, the effect of greater depth together with great resolution may be obtained by conical illumination. By this method of illumination, the structure of the specimen itself is employed as the means of producing shadows and shading, thus forming great contrast which gives the effect of depth. This method of illumination gives an image which is a natural one similar to ordinary images observed by the unaided eye.

Conical illumination is obtained by inserting one of a graduated series of conical stops into the opening of the vertical illuminator. For best results, conical illumination is combined with oblique illumination by a rack-and-pinion mounting. Trial of the various-sized stops will indicate the one best suited in any particular case.

While different methods of illumination present an appearance of greater depth, this must not be taken to imply that such methods solve the problems confronting the oil geologist.

For a more detailed account of methods of illumination, see chapter on Practical Photomicrography by Loveland and Trivelli.

Resolution.—The ability of a microscope to reveal detail to the eye depends not upon the magnifying power of an instrument but entirely upon the ability to distinguish between neighboring diffraction images of the points in the object. Since the total of these diffraction images constitutes the image viewed, it can be seen that the limit of resolution of the microscope depends upon the limit of resolution of two neighboring points.

It is well known that when light falls upon a narrow opening, a series of light and dark spaces can be seen instead of one light streak bordered by a dark shadow. A second source of illumi-

¹ Hanna has presented an interesting review of the literature on this subject to convince workers in petroleum geology of the futility of photographic attempts contrary to optical laws. HANNA, G. DALLAS, "The Photography of Small Objects," *Trans. Am. Micro. Soc.*, Vol. XLVI, No. 1, pp. 15-25, January, 1927.

nation would produce the same type of pattern. The two patterns, and, therefore, the two sources, can be distinguished (according to the criterion of Lord Rayleigh) if

$$\frac{\lambda}{a} = \alpha \quad (1)$$

Where λ is the wave length, a the width of the slit, and α the angular separation of the two diffraction maxima.

In the case of the simple microscope, which may be taken as illustrative of any type, if a be the diameter, f the focal length, and θ the angle subtended by the aperture at the focus, then one may write, to a close degree of approximation,

$$\frac{\frac{1}{2}a}{f} = \sin \frac{\theta}{2} \quad (2)$$

If an object of length is to be distinguished, and the limiting angle of resolution is α , from Eq. (1) above, the following diagram would represent the limiting condition



Since to distinguish the image R , the two ends of which would be required to subtend an angle α , the object E would also be required to subtend the same angle; therefore,

$$\frac{E}{f} = \sin \alpha = \alpha \quad (3)$$

since α is very small; or

$$\frac{E}{f} = \alpha = \frac{\lambda}{a} \quad (4)$$

It can be seen that the aperture of the "slit" in the case of a lens is a , its diameter. When the results from Eq. (4) are substituted in Eq. (2), there remains

$$E = \frac{\lambda}{2 \sin \frac{\theta}{2}} \quad (5)$$

If a material of index of refraction n is used, the length of focus in Eq. (3) becomes nf , and Eq. (5) may be expressed as follows:

$$E = \frac{\lambda}{2n \sin \frac{\theta}{2}} \quad (6)$$

From this it is apparent that the resolving power depends upon the wave length of the light used and upon the index of refraction of the medium in which the objective is immersed. It is also evident that to reduce the length which can be distinguished the methods open are to use shorter wave lengths of light and an immersion oil of very high index of refraction.

A slightly more general form for Eq. (6) would be

$$E = \frac{k\lambda}{2n \sin \frac{\theta}{2}} \quad (7)$$

since the Rayleigh criterion in the case of circular apertures is $1.22 \frac{\lambda}{a} = \alpha$, and since this criterion is approximate and varies slightly with different observers. k is a constant depending upon the form of aperture used.

As commonly stated, resolution is expressed as:

$$R = \frac{\lambda}{2N.A.}$$

the present limit for numerical aperture being about 1.65, and is obtained with the aid of alpha monobromnaphthalene ($n = 1.66$) as an immersion medium. Spark spectra employing the magnesium line, $280\mu\mu$, and the cadmium line, $277\mu\mu$, in conjunction with a quartz optical system including the illuminator, have been successfully employed in photomicrography.¹ An eye piece is employed which consists of a fluorescent screen viewed by a magnifier for focusing in this invisible range of wave lengths.

The limit to the detail which can be recorded with a given photographic material has been expressed as the distance by which two points of light must be separated on the sensitive film so that they will be recorded as two images and not as one.²

The Bureau of Standards states that the best resolution of plates examined by them was, in the case of an ordinary process plate, able to resolve lines the centers of which were 0.012 millimeter apart. The best orthochromatic-process plate examined

¹ LUCAS, FRANCIS F., "An Introduction to Ultra-violet Metallography," *Mineral Met. Pamphlet* 1,576-E, p. 7, June, 1926.

² DAVIS, RAYMOND, and F. M. WALTERS, JR., "Sensitometry of Photographic Emulsions and a Survey of the Characteristics of Plates and Films of American Manufacture," U. S. Bureau of Standards, *Scientific Papers* 439, May 5, 1922.

resolved lines 0.019 millimeter apart, and the best panchromatic-process plate, lines 0.018 millimeter apart.

Process plates are the most finely grained plates which can be easily obtained. The so-called *grainless emulsions*, such as the emulsion prepared with albumen, have not given sufficiently good results to warrant their use.

According to Sandvik,¹ any value of resolving power determined by any method employing a test object of the line type, as used in the above determinations by the Bureau of Standards, is quite meaningless unless accompanied by a definite specification of the ratio width of line:width of space. The direct relationship between the resolving value and this ratio has been definitely established by Sandvik. This variation is large, amounting, in some cases, to eightfold for ratio values ranging from 0.130 to 10.0.

Resolving power varies enormously with exposure. At low and at high exposure values, resolving power is relatively low, while a marked maximum is obtained at intermediate exposure values. This variation in resolving power may amount to 60 per cent (or more) of the maximum value.²

Other factors which affect the resolving power of a plate are irradiation and the spreading of the image due to the reflection of light in the film from one silver grain to another, development time, reducing agent, constitution of developing solution, etc.

Wright³ directs attention to three factors which are of importance in high-power-microscope work, namely, (a) the use of a polarizing prism to eliminate that part of the field light which does not contribute to the diffraction pattern in the image and hence tends to reduce the contrast and to decrease the sharpness and crispness of the image; this phenomenon arises because diffracted beams which emerge from gratings whose interval is of the order of magnitude of $\frac{1}{2}$ wave length of light are sensibly polarized in a plane normal to the lines of the grating; (b) a diaphragm of the rectangular type is recommended for use in the

¹ SANDVIK, OTTO, "On the Measurement of Resolving Power of Photographic Materials," *Jour. Optical Soc. Am.*, Vol. XIV, No. 2, pp. 169-177, February, 1927.

² HUSE, K., "Photographic Resolving Power," *Jour. Optical Soc. Am.*, Vol. I, p. 119, 1917.

³ WRIGHT, F. E., "The Contrast Sensibility of the Eye as a Factor in the Resolving Power of the Microscope," *Jour. Optical Soc. Am.*, Vols. II-III, Nos. 3-6, May-November, 1919.

image plane of the eye piece in order to cut out all light except that from the particular object under examination; and (c) the importance is emphasized of a field intensity of illumination approaching that of daylight and best adapted for the eye at any particular time; the simplest method for securing this is by means of a substage polarizer in conjunction with the polarizing prism; the polarizer can be rotated, and thus, the intensity of illumination of the field varied.

The importance of contrast to resolution does not appear to be fully appreciated. The relation of width of line: width of space in the test object to resolution of photographic material referred to above probably results from differences in contrast. The importance of contrast is better appreciated if this is true, since it was determined, in some cases, to amount to as much as eightfold.

An interesting example of the effect of contrast is afforded by the method of studying coke devised by Rose of the Mellon Institute. The pores of the coke are filled with plaster of paris and a section of coke thus prepared yields great contrast due to the differential absorption of poorly absorbing plaster and strongly absorbing coke.

One of the factors which prevent attainment of the theoretical limit of resolution is the great loss of intensity produced by absorption; hence, any means which tend to counteract this effect will give greater resolution.

For a more complete treatment of the resolving power of the microscope, consult such standard works as Drude's "Optics." Berek has recently published an excellent paper in German entitled, "The Development and the Present State of the Theory of the Microscopic Image."¹

Application of Polarized Light to Opaque-mineral Determination. Several investigators² have discussed the subject of the

¹ BEREK, M., *Proc. Soc. Advancement Natural Sci.*, Marburg, 1927.

² WRIGHT, F. E., "Polarized Light in the Study of Ores and Metals," mathematical study, *Proc. Am. Phil. Soc.*, 1919.

Idem., "Examination of Ores and Metals in Polarized Light," *Mining Met.*, 158, February, 1920. For earlier work, see references given by Wright. Of the earlier workers J. Koenigsberger, K. Endell, and H. Hane-mann are especially important.

BEREK, M., "Basis for the Determination of Minerals on the Ground of the Optical Phenomena Which They Present in Vertical Incident Light Both Natural and Polarized," *Manual for the Microscopic Determination*

application of polarized light to the study of opaque minerals. A complete summary of the work cannot be attempted here.

Determination of the degree of anisotropism of a polished opaque mineral is accomplished by (a) detection of the difference in intensity of the reflected components of light; (b) determination of the rotation of the plane of polarization of incident, plane-polarized light waves after reflection from the mineral.

In (a), if the reflected light waves are plane polarized, one of the components is more intense than the second and the excess of intensity in one direction gives rise to a certain amount of polarized light in the reflected light waves. An arrangement is used which includes a photometer. The polarized light, in a certain arrangement of the apparatus, enters only one field of the photometer, and, thus, measurements are made possible which will indicate the amount of polarized light present. For details of the method, see article by Wright.

The most sensitive method available is that by which the degree of anisotropism is determined by the amount of angular rotation of the analyzer required to produce equal intensity of illumination in the adjacent halves of the Wright bi-quartz wedge-plate.

To determine the amount of rotation by this method, the microscope is arranged as follows: A research model petrographic microscope, which permits measurements of the rotation of the analyzer, is equipped with an opaque illuminator. The usual form of the cap analyzer does not possess a sufficiently great graduated arc for accurate measurement of the rotation. First of all, the position in which the nicol prisms are accurately crossed must be determined. For method, see page 11.

The polarizer can be either fitted into the front of the opaque illuminator or held upon a stand in front of it. The plane of vibration of the polarized light from the polarizer is brought accurately parallel to the plane of incidence of the reflecting surface of the prism or glass plate in the opaque illuminator.

and Investigation of Ores and Ore-dressing Products Especially in Reflected Light, Hans Schneiderhöhn, 1922.

SAMPSON, EDWARD, "Note on the Determination of Anisotropism in Metallic Minerals," *Econ. Geol.*, Vol. XVIII, No. 8, December, 1923.

SCHLOSSMACHER, K., "Course of Quantitative Work in Ore Microscopy," *Fortschritte Mineral. Krist. Petr.* 9, pp. 161-184, 1924.

GLAZER, L. C., "Metallography in Polarized Light," *Z. tech. Physik* 5, pp. 253-260, 1924.

The extinction positions due to a rotation of the analyzer are best obtained with the Wright bi-quartz wedge-plate. This consists of two plates of quartz cut normal to an axis and of specified thickness, one of right-handed and the other of left-handed quartz, each with a quartz wedge of opposite sign of rotary polarization. The effect of this combination is to produce zero rotation in each half-wedge where plate and wedge have the same thickness, and as the wedge is inserted or drawn out from this point of zero rotation the angle of rotation increases proportionately and in a positive sense on one side of the junction line of the combination and in a negative sense on the opposite half. This combination wedge, which is introduced at the focal plane of the ocular, divides the field under crossed nicols into two halves the intensity of color of which at any instant is equal provided no intervening crystal plate is present or is rendered inactive by the parallelism of its ellipsoidal axis with the principal planes of the nicols. As soon as the crystal is turned even a very small angle out of this position, the intensity of illumination of the two fields is no longer equal. By inserting or withdrawing the combination wedge, the most advantageous angle of rotation in the two fields can be obtained, so that the difference in intensity between the two halves is more apparent.¹

The sources of error in this determination follow:

1. Character of polished mineral surface.
2. The surface of the polished section must be exactly normal to the optical axis of the microscope.
3. Polarization produced by objectives.
4. Aperture of the illuminating cone of light.
5. Orientation of mineral.
6. Angular deviation from the azimuth of the plane of polarization of the incident beam.
7. Elliptic polarization from prism or plate of opaque illuminator as well as from curved lens surfaces of objective or other parts of the optical system.
8. Rotation of plane of polarization produced by the oblique end surfaces of nicol prisms of usual form.
9. Dispersion of light.

The polished mineral surface must be free from scratches which allow refraction of light and show polarized reflection. A

¹ WRIGHT, F. E., "Measurement of Extinction Angles in Thin Section," *Am. Jour. Sci.*, Vol. XXVI, No. 154, p. 377, October, 1908.

natural fibrous structure may thus be a source of error. It is, of course, theoretically possible to obtain reciprocal compensation of such reflection, providing the scratches are equally distributed in all directions.

The surface effects produced by polishing processes may influence the determination of optical character. Evidence has been obtained that the more metallic minerals, at least, may become covered by an amorphous film by polishing processes. Apparently, it is impossible entirely to eliminate the production of a surface film by present polishing methods; therefore, it becomes essential to insure that the film produced possesses a minimum thickness. The ellipticity of reflected light is profoundly affected by the presence of surface films, regardless of certain published statements which indicate that the magnitude has been overestimated. Amorphous material is isotropic, and if a film of amorphous material should attain sufficient thickness, it is possible that anisotropic effects would be masked. Surface-film effects are also known to produce distinct anisotropic effects from isotropic minerals.

The method of polishing recommended to produce a minimum of surface effects is an old one, presented in detail by Guthrie:¹ A hard, structureless base upon the grinding and polishing wheels was found to lessen the undesirable film, whereas a cloth-covered disc, using any of the various cloths which have been recommended, produces a much thicker film. A paraffin-covered brass disc was adopted. The disc was prepared by pouring molten paraffin upon the disc, the paraffin being prevented from running off by a band of tin wrapped around the periphery. After solidifying, the disc was placed on the polishing machine and rotated under a straight-edge, thus dressing out the surface evenly. The slight "chatter" left in the paraffin appears to increase the effectiveness, especially by minimizing the "seizing" of the sample by the paraffin.

The abrasive is held in an ordinary glycerine-base soap solution made up with distilled water which serves to lubricate the sample so that it will not adhere to the wheel. The glycerine prevents the soap from precipitating out of the solution. In regard to abrasives, the writer has found the finest grade of optical emery followed by alumina or rouge,

¹ GUTHRIE, R. G., "Sample Preparation for High Power Photomicrography," *Trans. Am. Soc. Steel Treating*, March, 1925.

according to the hardness of the minerals involved, to give excellent results.

According to Schneiderhöhn,¹ objectives which are apparently free from polarization, when tested in transmitted polarized light by the most refined methods known, may be the source of serious error. In order to overcome this source of error, the objective should be rotated between crossed nicols in incident light from any isotropic reflecting surface, such as plain mirror glass. During a complete rotation of the objective, four positions of darkness will be observed; while in all other positions, the field will be more or less bright, gray, or colored. The positions of darkness are marked on the objective mount, and such positions used during observations.

A diaphragm to control the aperture of the illuminating cone of light is essential. If the aperture is too high, the rays of high angular aperture meet the specimen under such an angle that elliptical polarization will result. The aperture should always be kept as small as possible.

The orientation of a mineral might be a source of error in determining the rotation of the plane of polarization. If a section should be obtained which is normal to an optic axis, the rotation will be zero, and the mineral will appear isotropic.

The square-end type of prism, either Glan-Thompson or Ahrens, does not rotate the plane of polarization of transmitted light wave to the extent of the ordinary nicol and is to be preferred in accurate work. The polarizing prisms commonly attached to the reflecting microscope are the ordinary nicol type, and the rotary effect of the oblique faces must be considered as a source of error.

Dispersion of light if produced by an opaque mineral is a source of error. Different-colored rays are of different wave lengths; consequently, a measurement made by one colored light may not be correct for another, and sharp extinctions may not be obtained. In such cases, it is necessary to use monochromatic light.

It is, perhaps, unnecessary to state that objectives apparently free from polarization must be treated with extreme care to avoid shocks or sudden changes of temperature.

¹ SCHNEIDERHÖHN, HANS, *Manual for the Microscopic Determination and Investigation of Ores and Ore-dressing Products Especially in Reflected Light*, 1922.

In order that a better understanding of the subject of elliptic polarization may be received, a brief introduction to the subject is presented in the following pages.

Introduction to the Subject of Elliptic Polarization of Light.—

Regardless of whether the actual propagation of light takes place in the form of a wave motion or not, this viewpoint lends itself readily to a discussion of polarized light.

Light as ordinarily received from a self-luminous body exhibits no one-sidedness in its properties and is said to consist of vibrations at every conceivable angle, the vibrations being transversal, that is, taking place in a direction perpendicular to the direction of propagation.

When light is passed through a calcite crystal in a direction other than along the optic axis, two images of one luminous source can be seen. This would mean that calcite would have two indices of refraction. The index of refraction, however, is dependent upon the ratio of the velocity of light in air: the velocity within the medium. Double refraction, therefore, indicates that the light has been split into two parts by the properties of the crystal and that to the motion of each of these parts there is imposed a definite resistance by the crystal.

It has been found that, if the crystal be rotated about the path of the light undergoing the least deviation, the second image formed in the case cited above will revolve about the first. A consideration of these and similar facts has caused physicists to give the explanation that the light in each of these images consists of vibrations in one plane. One of the two images is formed by the *ordinary* ray, the second by the *extraordinary* ray.

The ordinary Nicol prism is so constructed that it allows but one of these rays, the extraordinary ray, to pass and, therefore, furnishes plane-polarized light available for testing the effect of any material upon plane-polarized light. It is readily seen that a second Nicol prism, similarly oriented with respect to the first, would allow the extraordinary ray to pass but that if it were rotated through a certain angle (90 degrees), the ordinary ray would be the only one permitted to pass; but since there would be no ordinary ray, in this case, the result of *crossed* Nicols upon parallel polarized light is darkness.

No behavior of light has been noted which would indicate a difference in wave shapes. The study of polarized light, there-

fore, reduces to the consideration of the vibrations perpendicular to the direction of propagation. A convenient method of representation of the vibration in a single plane is a straight-line vector \longrightarrow , which can be thought to represent the path of an *ether* particle, as it rides on its portion of the light wave much as a cork would float upon a water wave.

Suppose that there should exist a medium of such nature that the ordinary incident light would be divided into two rays which were polarized in planes separated by an angle of 90 degrees. In addition, suppose that conditions were such that no division of the two emergent beams could be detected. In this case, there would be the possibility of three types of light: (a) plane polarized, (b) circularly polarized, and (c) elliptically polarized.

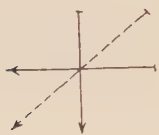


FIG. 2.



FIG. 3.



FIG. 4.

If the two component vibrations were in the same phase (by *phase* is meant the position in the vibration cycle) or at a phase difference of any multiple of π , the result would be plane-polarized light (see Fig. 2). The dotted line represents the resultant vibration.

If the two component vibrations were π ($2\frac{1}{4}\lambda$) or any odd multiple of π out of phase, the resultant would be a circular vibration (see Fig. 3).

If the two components were out of phase by an amount different from the positions already mentioned, the resultant would be an elliptical path for the *ether* particle. The light would be termed *elliptically polarized light* (see Fig. 4).

The analysis of elliptically polarized light can be accomplished by following a procedure exactly the converse of the above reasoning. Since an elliptically polarized vibration is composed of two component plane-polarized vibrations, it may be decomposed into two plane-polarized vibrations. Given a beam of elliptically polarized light, the elliptical vibration may be said to be due to a resultant of two plane-polarized components taken along any set of axes. If the major and minor axis of the

ellipse be taken, the result is indicated in Fig. 5. Since the components are $\pi/2$ apart, if, by some means, the vibration in the direction BB' could be changed in phase so that this wave at B would be in the same phase as at A , a plane-polarized beam would result represented by DD' in Fig. 5. Such a procedure is a practical one.

Thin sheets of mica can be split until there is a $\frac{1}{4}\lambda$ ($\pi/2$) phase difference between two plane-polarized beams transmitted along its two axes, the axes being perpendicular to each other.

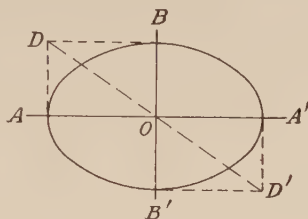


FIG. 5.

To illustrate, suppose a Nicol-prism polarizer and a Nicol analyzer were mounted in line and the analyzer were rotated until the prisms were crossed. Next, suppose a $\frac{1}{4}\lambda$ plate to be mounted perpendicular to the path of the light, which must be monochromatic (since $\frac{1}{4}\lambda$ retardation for one color may, of course, not be $\frac{1}{4}\lambda$ retardation for any other). If the $\frac{1}{4}\lambda$ plate be rotated until darkness is observed at the analyzer, the following conditions exist:

1. Plane-polarized light leaves the first Nicol and enters the $\frac{1}{4}\lambda$ plate.

2. The planes of transmission of the $\frac{1}{4}\lambda$ plate are, respectively, in the plane of the polarized light and perpendicular to it.

3. The analyzer is so set that the oncoming polarized light is extinguished.



FIG. 6.

Next, a doubly refracting crystal is placed between the polarizer and the $\frac{1}{4}\lambda$ plate, as in Fig. 6; A is polarizer, B is crystal, C is $\frac{1}{4}\lambda$ plate, D is analyzer. Elliptically polarized light will, in general, be produced by the crystal B . It will be found that to obtain darkness again at the analyzer D it will be necessary to rotate both the $\frac{1}{4}\lambda$ plate C and the analyzer D . In the accompanying Fig. 7, the ellipse represents the vibration. The lines AA' and BB' represent the component perpendicular

plane-polarized vibrations and represent, also, the position of the transmission planes of the $\frac{1}{4}\lambda$ plate when the analyzer is set for extinction. The change in position of the $\frac{1}{4}\lambda$ plate, therefore, locates the position of the principal axis of the ellipse of vibration. Now, the equivalent plane-polarized beam extinguished by the analyzer in its new position is the vibration along GG' , so the plane of extinguishment of the analyzer is along OE , while the plane of transmission is parallel to OG . The ratio of $GA':OA'$, therefore, the ratio of the axis of the ellipse, is equal to the tangent of the angle between the axis of trans-

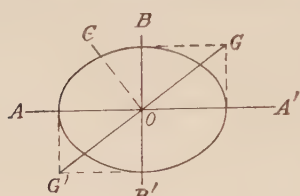


FIG. 7.

mission of the $\frac{1}{4}\lambda$ plate and the axis of transmission of the analyzer.

The same principle is used when polarized light is reflected from the face of an anisotropic crystal. In this case, it must be remembered that the amount of elliptical polarization measured is affected by the depth to

which the reflected elliptically polarized rays penetrate the crystal.

Use of Microscope in Microchemical Analysis.—Physical constants, such as those obtained by means of petrographic and x-ray study, are influenced by chemical composition. Atomic substitution, which is the rule rather than the exception among minerals, is liable to be accompanied by a great change in physical constants. It is, therefore, essential to connect physical data with chemical composition. Ore minerals are common as finely disseminated, intermixed forms with which even microchemical analysis is difficult of application. It is essential when dealing with an unknown finely disseminated mineral to obtain an uncontaminated sample for analysis. Several methods have been devised for preventing contamination. The methods in common use to obtain a minute quantity by scratching with a bent needle attached to a holder held in the hand or by means of a diamond point used as a hand drill are obviously crude, and in their use no attention is given to the possibility of contamination in the third dimension.

Jaggard¹ described a microsclerometer, stating that the instrument "suggests the possibility of an adaptation by which

¹ JAGGAR, T. A., JR., "A Microsclerometer for Determining the Harness of Minerals," *Am. Jour. Sci.*, Vol. VI, pp. 399-412, December, 1897.

perhaps chemical tests may be applied directly to the dust in the boring" (p. 412).

Graingg¹ devised a small boring contrivance placed in the optical axis of the microscope for obtaining drillings to be used in microanalysis.

The complicated microsclerometer of Jaggar is obviously not adapted to microchemical work, while Graingg's contrivance presents difficulties of a mechanical nature in attempting to center the drill point accurately. Fairbanks² devised a micro-drill to be used with microscope which permits accurate centering, measures depth, and has proved satisfactory in routine work.

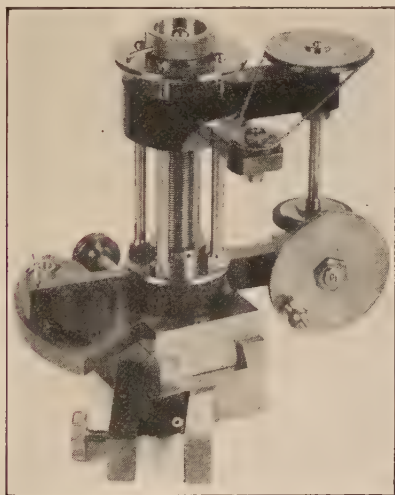


PLATE I.—Microdrill for microchemical analysis.

It is obvious that powder from the more finely disseminated minerals cannot be obtained uncontaminated. In such cases, an uncontaminated sample is obtained from the inclosing mineral and compared with a sample of the disseminated mineral contaminated with the host. The composition of the inclosing mineral being known, it would not be difficult to determine the nature of the disseminated mineral, if it were not for the fact that

¹ GRAINGG, B., "Zur. anwendung metallographischer Methoden auf die mikroskopische Untersuchung von Erzlagerstätten," *Metall. u. Erz.*, Vol. XII, pp. 191-3, 1915.

² FAIRBANKS, ERNEST E., "Microchemical Analysis and Its Application in the Determination of Low Grade Ores," *Reports of Investigations* 2,613, U. S. Bureau of Mines, June, 1924.

identical elements may be present in each. Thus a quantitative microchemical analysis is necessary to determine the true character in difficult cases.

The ratio of silver microcrystals:antimony microcrystals, for example, from the following minerals should serve to distinguish one from the other:

Stephanite.....	5Ag ₂ S:Sb ₂ S ₃
Polybasite.....	8Ag ₂ S:Sb ₂ S ₃
Polyargyrite.....	12Ag ₂ S:Sb ₂ S ₃

Quantitative methods applied to microchemical analysis are not so simple as they might appear, but the method seems to have future possibilities.

The effect of interfering substances, more common when dealing with opaque minerals than in other cases, is not sufficiently understood. If petrographic methods are applied to microcrystals, however, their identification can be made certain when of sufficient size (for an additional method see chapter on Dielectric Methods).

Qualitative Determination of Hardness with Microscope.—Light-lines similar in appearance to the Becke line as used in refractive index determinations are observed when the tube of the microscope is moved out of sharp focus on the boundary between two opaque minerals. The line moves from the harder to the softer mineral upon raising the tube of the microscope. This appears to be an old method, although it does not seem to be in general use at the present time. It has been mentioned by Schlossmacher, Kalb, and others.

CHAPTER III
CRYSTAL ANALYSIS BY MEANS OF X-RAYS
BY WHEELER P. DAVEY
APPARATUS

In determining the structure of crystals, it is very desirable that the experimenter be able to put a maximum of attention on the problem at hand and a minimum of attention on the operation of his apparatus. To this end, the research laboratory

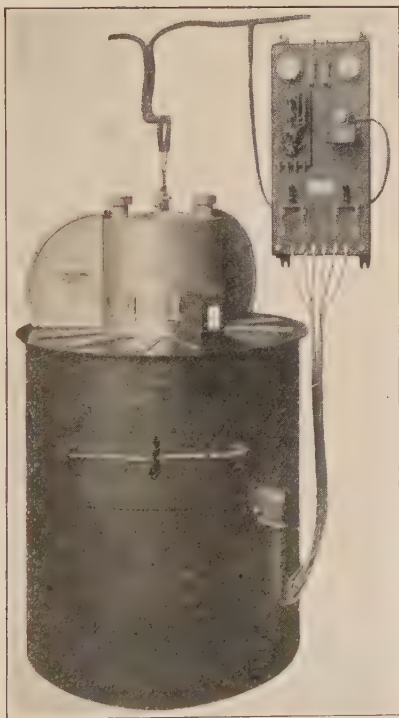


FIG. 1.—X-ray diffraction apparatus.

of the General Electric Company has designed and placed on sale a completely coordinated X-ray diffraction apparatus (U. S. Patent 1546349) which may be used directly for either the Laue or the *powder* methods of crystal analysis. By using certain

accessory parts, the apparatus may also be used for the Bragg method. When used for the powder method, the apparatus furnishes the experimenter, without the necessity of computation of any sort, with a systematic statement of interplanar spacings in the crystal, starting with the largest spacing (limit of the apparatus 6.0\AA .) and ending with the smallest spacing (limit of the apparatus 0.550\AA .). The spacings between the limits of 2.000\AA . and 0.550\AA . may be obtained easily to the third decimal place in Angstrom units, *i.e.*, to 10^{-11} centimeters. It is with these spacings that the crystal analyst has to do.

The apparatus (Fig. 1) consists of

1. A supporting table and cylindrical slit holder.
2. A water-cooled molybdenum-target Coolidge X-ray tube.
3. A transformer and stabilizer specially designed for half-wave operation.
4. A switchboard with meters, voltage control, and protective devices.
5. A slit system which allows 12 diffraction patterns to be taken at once.
6. Cassettes for holding the specimens and photographic film.
7. A *range finder* to assist in adjusting the position of the X-ray tube.
8. A scale for interpreting the X-ray diffraction patterns directly in terms of the interplanar spacings of the crystal.

The Table and Cylinder.—The table top *T*, in Fig. 2, consists of a disc of steel $\frac{1}{2}$ inch thick, provided with 12 radial guides for the cassettes. A hole is cut in the center. In this hole is fitted a metal cylinder *D* which acts as a support for the slit system and at the same time, because of the long wave length of the X-rays employed, provides X-ray protection for the investigator. Twelve rectangular openings at the level of the slit system allow the rays to reach the glass tubes containing the specimens. Under each of these openings is another opening, which may be used, when desired, for calibrating the photographic film. The top of the cylinder is closed by a flat brass cover (Fig. 3) which also acts as a rigid support for the anode end of the Coolidge tube. The cathode end of the tube hangs free. The cylinder and cover are machined so that the axis of the tube automatically coincides with the axis of the cylinder. A nut *KN* allows a vertical adjustment of the tube along the

axis of the cylinder. The underpart of the table is enclosed by a cylinder of heavy sheet iron, reenforced with angle iron, and

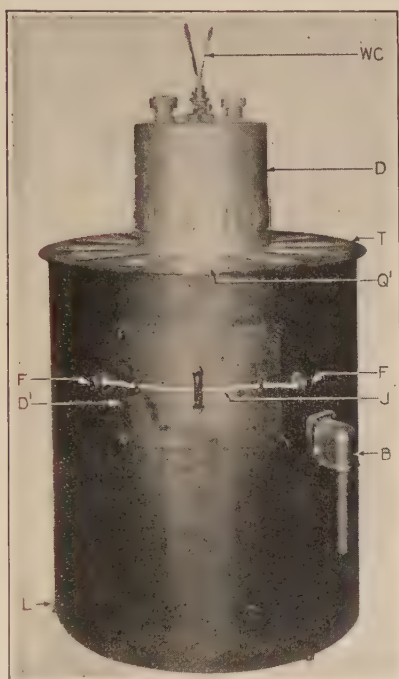


FIG. 2.—Case, table top and cylinder X-ray diffraction apparatus.

provided with a door (D' , in Fig. 2) to give access to the high-tension transformer which sits inside. The primary circuit of

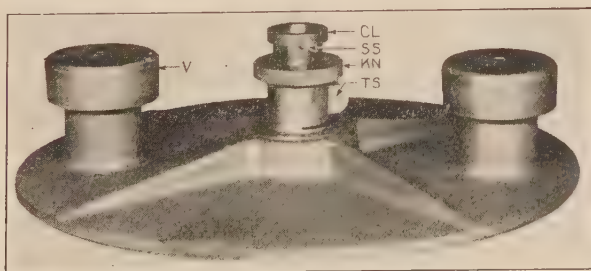


FIG. 3.—Tube holder and height adjuster X-ray diffraction apparatus.

the transformer (Fig. 4) is carried across the front of this door in such a way that the door cannot be opened without opening

the primary circuit, as shown in *J*, of Fig. 2. In this way, when the X-ray tube is in operation, the operator is protected from accidental contact with the high potential.

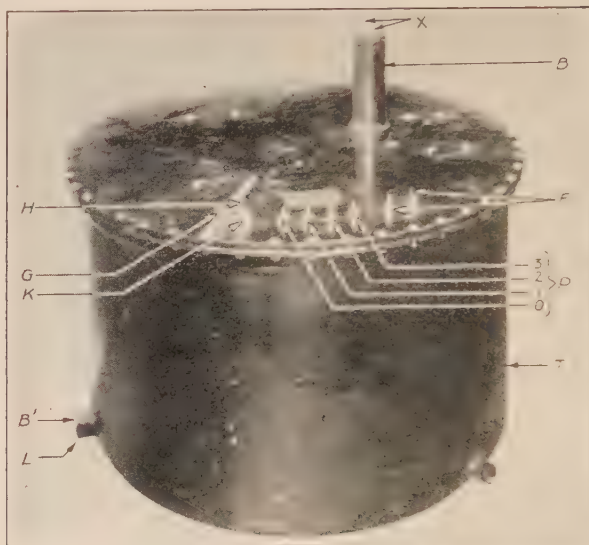


FIG. 4.—30 kv. transformer. X-ray diffraction apparatus.

The Tube.—The X-ray tube is of the usual Coolidge type but with a special water-cooled anode. This anode consists of a hollow copper rod at the end of which is fastened a Mo button. The face of the Mo button is perpendicular to the axis of the tube, so that X-rays may be taken off all the way around the



FIG. 5.—Diagram of water-cooled Coolidge tube.

anode. The maximum allowable filament current is 4.75 amperes. The maximum tube voltage for efficient production of Mo characteristic rays is 30 kilovolts r.m.s. At this voltage, the tube current should be about 25 milliamperes but will vary from 20 to 25 milliamperes from one tube to another. The dimensions of the tube are shown in Fig. 5.

The radiation from the tube is filtered through filters of zirconium dioxide, each having 0.05 gram of ZrO_2 per cm^2 built into the cassettes. The filter eliminates most of the *white* (general) radiation, makes the Mo β doublet negligible, and eliminates a large part of such characteristic rays as may be given off by the specimen itself. The diffraction pattern, as recorded on the photographic film, is, therefore, caused by the Mo α doublet, which consists of two wave lengths which differ from each other by less than 1 per cent. The optimum direct-current voltage for the production of Mo $K\alpha$ is 28 to 30 kilovolts,¹ but operation on alternating current at 30 kilovolts maximum makes the time required for a satisfactory film so long that it is prohibitive for ordinary work. Experience shows that 30 kilovolts r.m.s. is about the maximum voltage at which the white radiation may be filtered easily from the molybdenum characteristic rays. For this reason, it was adopted as the standard operating voltage for the apparatus.

The Transformer and Stabilizer.—The Coolidge tube is operated directly from a transformer without any additional rectifying device. This necessitates a special design of transformer, for, although the secondary must apply power only on one-half of the wave, the voltage of the inverse half-wave must not greatly exceed that of the useful half-wave, otherwise, there will be considerable trouble from corona during the inverse half-wave. The use of other types of transformers with the X-ray diffraction apparatus is not recommended. The transformer has only one developed terminal, the other end of the secondary being grounded through the milliammeter. A protective spark gap is provided across the milliammeter circuit, so that the meter is always safe to handle even if one of its connections is broken. The filament of the Coolidge tube is heated by a step-down transformer whose secondary is at the potential of the high-potential end of the 30-kilovolt transformer. Both ends of this coil, as well as the high-potential end of the 30-kilovolt transformer are brought out through the high-potential terminal. A Victor stabilizer,² automatically lowers the filament temperature in case of excessive discharge currents through the

¹ HULL, A. W., "A New Method of Crystal Analysis," *Phys. Rev.*, Vol. X, 1917, p. 661.

² KEARSLEY, W. J., JR., "A New Type of Stabilizer for Use with the Coolidge Tube," *Jour. Radiology*, July, 1921.

tube. Figure 6 gives a diagram of the connections. The high-potential filament circuit goes directly to the cathode of the Coolidge tube which hangs directly above. The anode of the tube is in electrical contact with the table top, as described above, so that the circuit is completed by the grounded metal table and the milliammeter back to the transformer. In this way, the high potential is entirely surrounded by grounding metal.

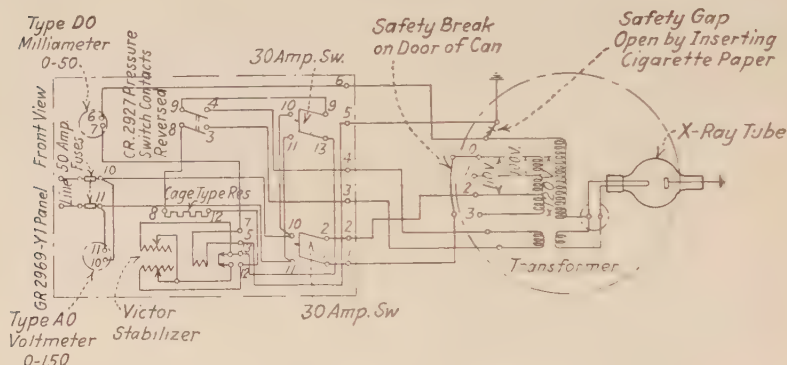


FIG. 6.—Connection diagram of X-ray diffraction apparatus.

The Switchboard.—The switchboard (Fig. 7) contains the customary fuses W , the operating switches $M'X'$, the Victor stabilizer $XX'L'Y$, a voltmeter V for reading the primary voltage, a milliammeter U , and a pressure-stat $K'P'$. This pressure-stat is connected to the outlet end of the water-cooled anode of the Coolidge tube. In case the water pressure falls too low, the pressure-stat opens the primary circuit of the filament transformer, thus protecting the tube from being burned out. The water pressure at the inlet end of the tube should be not less than 25 nor more than 80 pounds per square inch. In setting up the apparatus, enough resistance to the flow of water at the outlet should be provided so that the pressure-stat opens the filament circuit when the flow of water is less than 1 quart per minute.

The apparatus is supplied to operate on line voltages lying between 100 and 120 volts. A 2:1 transformer can also be supplied if required, so that line voltages from 200 to 240 volts can be used. The maximum variation in line voltage should preferably not exceed 2 per cent. This means that, if possible, the appa-

ratus should be connected to the lighting circuit of a commercial central station. It is essential that the frequency of the power source be constant. The apparatus can be furnished for either 50 or 60 cycles. The power consumption is about $2\frac{1}{2}$ kilowatts.

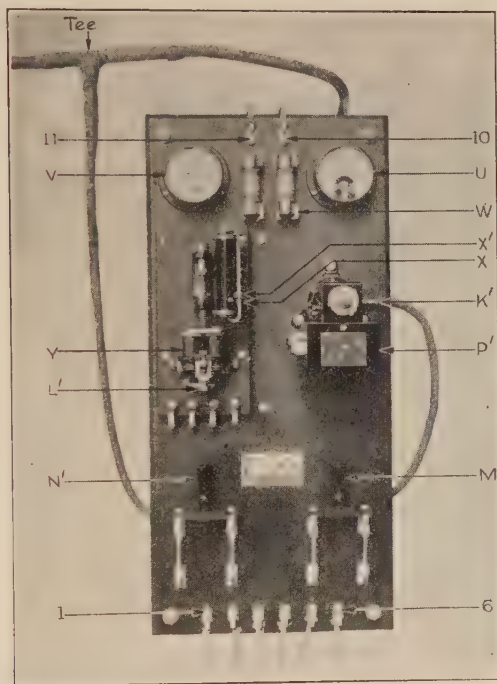


FIG. 7.—Switchboard for X-ray diffraction apparatus.

The Slit Assembly.—The slit assembly originally employed is shown in Fig. 8. It consisted of 12 radial-slit systems composed of three slits each. In each slit system, the two slits nearest the source of X-rays defined the beam. The third was wide enough to miss the primary X-ray beam and served to cut off the diffraction pattern produced by the edges of the second slit. The whole slit assembly was formed on the surface of a cone whose basal angle was about 4 degrees. In this way, each of the 12 slit systems utilized the full projection of the focal spot of the Coolidge tube. In order that the slits might be brought up close to the X-ray tube without danger of puncturing the tube, the first slit was insulated from the other two by being hung from a sheet of plate glass.

The slit assembly has recently been redesigned by the research laboratory of the General Electric Company to permit the use of several types of slits interchangeably. This increases the

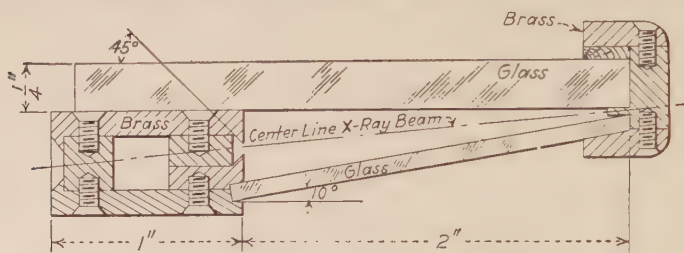


FIG. 8.—Diagram of original slit system.

usefulness of the apparatus many fold. The new slits (see Fig. 9) are made of a bakelite and litharge mixture which is an

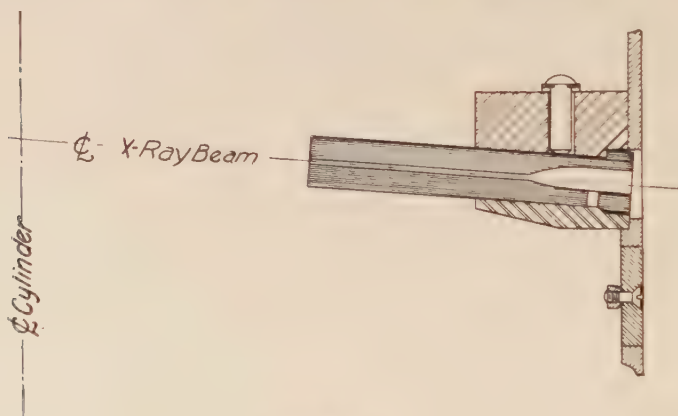


FIG. 9.

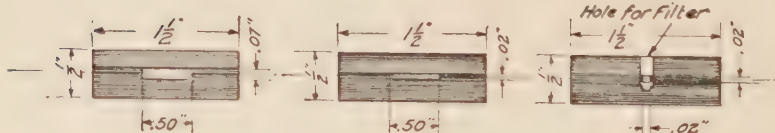


FIG. 10.

FIG. 11.

FIG. 12.

FIGS. 9-12.—Slit system of X-ray diffraction apparatus.

insulator and quite opaque to the X-rays employed. Blocks about 3 inches long are made of this material. Starting from the end nearest the X-ray tube and running in a radial direction

from the axis of the X-ray tube, a hole is cut in each block. This hole is about 2 inches long and serves the purpose of the first two slits of the original slit system. For the remaining inch the hole is considerably enlarged, so that its cross-section is larger than that of the primary X-ray beam. The end of this enlargement farthest from the X-ray tube takes the place of the third slit of the original slit system. By varying the cross-section of the hole, three types of slits are provided. These give beams 0.06 by 0.50 inch ($1\frac{1}{2}$ by $12\frac{1}{2}$ millimeters), 0.02

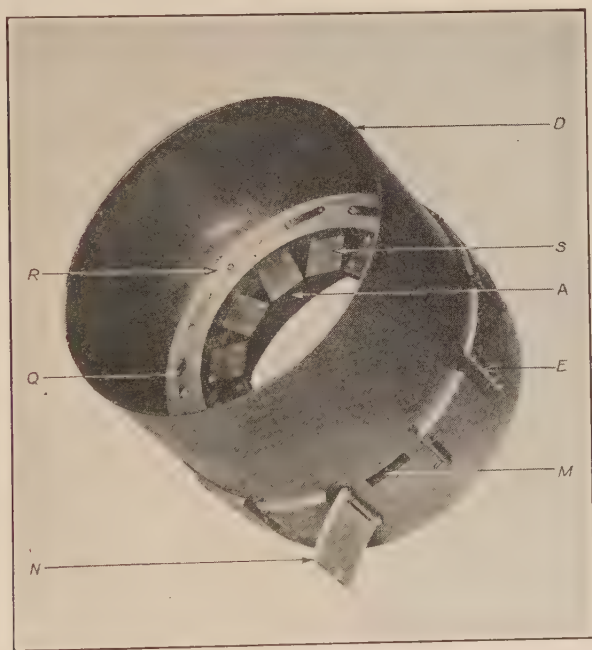


FIG. 13.—Cylinder and slit system ring with slits in place. X-ray diffraction apparatus.

by 0.50 inch ($\frac{1}{2}$ by $12\frac{1}{2}$ millimeters), and 0.02 by 0.02 inch ($\frac{1}{2}$ by $\frac{1}{2}$ millimeter), respectively. The first of these (see Fig. 10) gives a beam identical with that given by the original slit system. It is wide enough completely to bathe a narrow specimen with X-rays, so that the width of the lines in the diffraction pattern is determined primarily by the size of the specimen used. The second type of slit (see Fig. 11) gives a narrow beam which may be sent through a sheet of thin metal foil or other substances fairly transparent to the rays. The

width of the slit primarily determines the width of the lines in the diffraction pattern. The third type of slit (see Fig. 12) is practically a *pinhole* slit. It is intended for work on the effect of mechanical working upon the orientation of crystal fragments, etc. In such work it is not usually convenient to have a filter next to the photographic film. A small hole is therefore provided in the bakelite-litharge block by means of which a tiny ZrO_2 filter may be inserted across the pinhole slit. If the filter is removed from the hole, the slit is immediately made available for the Laue method of crystal analysis. The pinhole slit requires a special type of cassette which is quite different from the one described below. Four slits of each sort are normally provided with each X-ray Diffraction Apparatus. Since they are all interchangeable, additional slits of any one of the three types may be used if occasion requires.

The whole slit assembly is enclosed in a housing (see Fig. 13; this is the D of Fig. 2) which is substantially opaque to the X-rays used. Every effort has been made to make the apparatus safe from the standpoint of high voltage and X-rays. It is evident, however, that the manufacturers have no control over the way in which the apparatus is used in the hands of the purchaser. For this reason, they cannot guarantee the adequacy of the X-ray protection but request the user to test the safety of the apparatus himself under his own operating conditions.

The Cassettes.—The cassettes, one of which is illustrated in Figs. 14a and 14b, serve not only as holders for the films but also as holders for the specimens.

A strip of thin black celluloid is fastened to the cassette in the form of an arc 8 inches in radius, with the specimen at the center. The photographic film is held against this by a wide, flat, brass spring which is drawn up tight by a screw. A light-baffle over the spring prevents the film from becoming light-struck. The most satisfactory film for X-ray diffraction work seems to be the Eastman Dupli-tized X-ray film, $17\frac{1}{8}$ by 16 inches.

The design of the cassette is such that the user may insert an *intensifying screen* next to the photographic film if he wishes. The best screens now on the market will cut in half the time of taking the diffraction pattern. The use of screens introduces other difficulties, such as the trouble of avoiding dirt and stains on the screen, changes in the intensities of lines in the diffraction

patterns, etc. For this reason, the use of intensifying screens cannot be recommended for all kinds of work.

A staircase of copper is placed as an absorber in the path of the zero beam. In this way, there is always on the film some part of the zero line which has an exposure comparable to that of the first lines on the diffraction pattern. A Mo staircase is provided below the zero beam for calibrating the photographic film.

A septum in the median plane of the cassette divides it into two symmetrical chambers, so that diffraction patterns of two

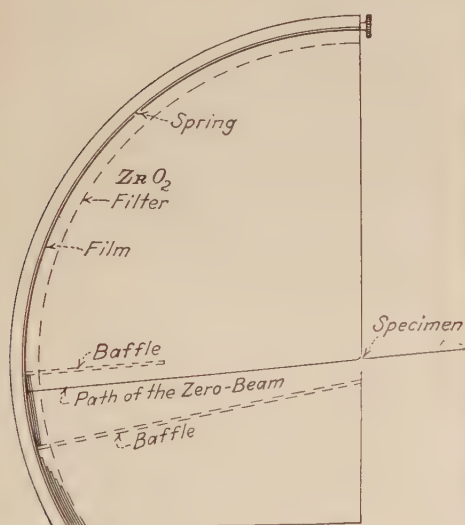


FIG. 14a.—Cassette.

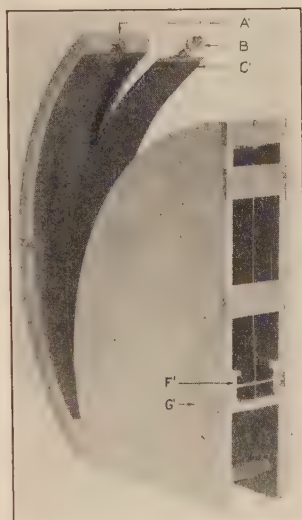


FIG. 14b.—Cassette for X-ray diffraction apparatus.

substances may be taken on the same film for purposes of comparison.

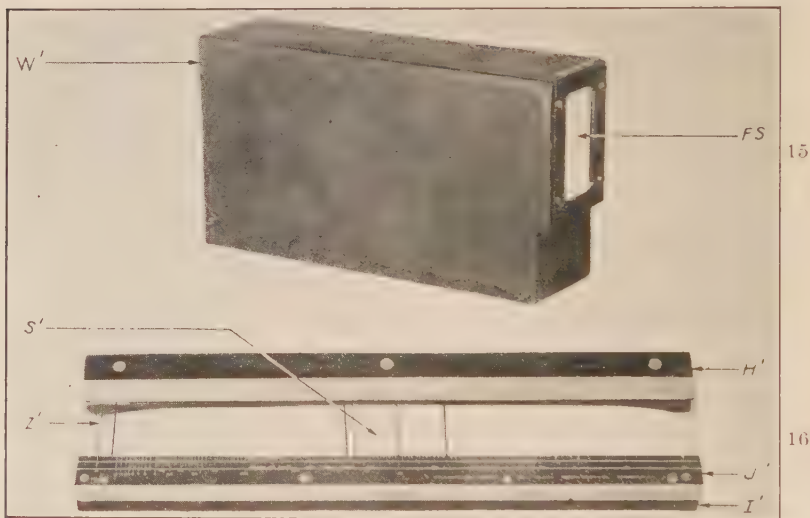
The Range Finder.—A *range finder* (Fig. 15) is provided for adjusting the height of the Coolidge tube. It is built to fit the guides on the table top so that it may be slipped into place opposite any one of the 12 slits. A tungsten wire, fastened by the screw *W'*, acts as the *specimen*. A fluorescent screen, *FS*, is mounted at the outside end in a position corresponding to that of the film in the cassette. The screen is faced with glass as a partial X-ray protection to the operator. The Coolidge tube is at the proper height when the fluorescent screen shows

that the shadow of the tungsten wire is in the center of the zero line.

The Scale.—The photograph of the X-ray diffraction pattern looks much like the familiar picture of a line spectrum. Using the classical equation for diffraction,

$$n\lambda = 2d \sin \theta, \quad (1)$$

a scale (Fig. 16) has been calculated by which each line of the film may be directly interpreted in terms of the distance between the planes of atoms which produced the line. The apparatus has thus made a record of the diffraction pattern of the specimen and



FIGS. 15-16.—Range finder (above) and scale. X-ray diffraction apparatus.

has enabled the experimenter to record in Ångström units the spacings of all planes in the crystal which are more than 0.55Å. apart. Where a solution of the crystal structure can be found at all, it is usually possible to make a valid solution using only lines corresponding to interplanar distances of more than 0.80Å. When the doublet is resolved ($\lambda_1 = 0.712\text{Å.}$)($\lambda_2 = 0.708\text{Å.}$), the readings of the two lines as given by the scale will be in the ratio of 1:1.005. In such a case, the pattern is to be considered as showing a single line situated halfway between the two actual lines. The order of accuracy of readings of lines by means of the scale increases from the left-hand end of the scale (large values) to the right-hand end (small values). At 1.00Å. , it is of the

order of 0.1 per cent. The limiting feature is the accuracy of the investigator in estimating the center of the line on the film.

METHODS OF CRYSTAL ANALYSIS

There are three methods in common use for determining the structure of crystals. These are known as the *Laue*, *Bragg*, and *powder* methods. The first two have already been sufficiently described elsewhere. For the Laue method, see "The Structure of Crystals," by R. W. G. Wyckoff (Chemical Monograph series, Chemical Catalogue Company, 1924). For the Bragg method, see "X-rays and Crystal Structure," by W. H. and W. L. Bragg (Harcourt, Brace and Company, 1924). Both of these methods are also described by the present writer in a series of articles on "A Study of Crystal Structure and Its Applications," in the *General Electric Review*.¹

The importance of the powder method to the physicist, crystallographer, and metallographer justifies a detailed description here.²

The Powder Method.—The powder method³ may be used with any crystalline substance. It is the only method which can be used with that large class of substances which cannot be obtained easily in the form of perfect crystals of appreciable size. This class includes not only most metals and their alloys but also a large number of compounds. This method uses a beam of essentially monochromatic X-rays, as does the Bragg method; but instead of using perfect single crystals, it uses crystals which have been crushed to such a fine powder that the fragments have a random or chaotic orientation. Such a powder requires no rotation, for, since every atomic plane is present in every possible orientation, there must be some individuals from each family of planes which are oriented at the correct angle to diffract the monochromatic X-ray beam. If the volume of powder used is large enough and the fragments are sufficiently small, there will be, for any given family of planes, many individuals correctly

¹ DAVEY, W. P., *Gen. Elec. Rev.*, Vol. XXVIII, pp. 129, 258, 342, 1925.

² The following is adapted from the *Gen. Elec. Rev.*, Vol. XXVIII, pp. 586, 721, 1925; Vol. XXIX, p. 118, 1926.

³ HULL, A. W., Paper before *Am. Phys. Soc.*, October, 1916. *Phys. Rev.*, Vol. IX, pp. 84, 564, 1917; Vol. X, p. 661, 1917.

DEBYE, P., and P. SCHERRER, "*Nachr. Kgl. Ges. Wiss. Göttingen*" (1915-16); *Phys. Z.*, Vol. XVII, p. 277, 1916; Vol. XVIII, pp. 291, 301, 1917.

oriented, so that the combined effect for any one plane is much the same as might be expected from a large single crystal having the same orientation. Experimentally, it is found that, in most cases, the powder is fine enough if it will go through 200-mesh¹ bolting cloth and that it is of sufficient amount if it will fill a cylindrical container about $\frac{3}{4}$ millimeter in diameter and about 10 millimeters long, *i.e.*, if the total volume is about 5 cubic millimeters. Since every atomic plane in the powdered crystal has some representatives at the correct angle for diffraction, the whole diffraction pattern may be photographed simultaneously.

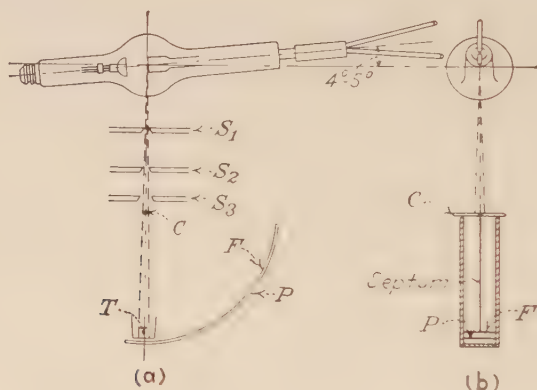


FIG. 17.—Schematic diagram of General Electric X-ray diffraction apparatus
(a) View from top. (b) View from side.

The time required to obtain a satisfactory record of the diffraction pattern varies from 5 to 12 hours for substances like NaCl to 70 hours or more for substances like CuCl and CsI. To a great extent the time required depends upon the physical condition of the crystal. The diffraction pattern may be interpreted in terms of the interplanar distances in the crystal by means of the scale shown in Fig. 16 which is calibrated in Angstrom units. If the crystal happens to belong to the cubic, tetragonal, orthorhombic or hexagonal systems, its structure may be interpreted directly from these interplanar distances by means of charts shown below, aided when necessary by the Theory of Space groups.

Experimental Technique of the Powder Method.—The X-ray tube, slits, and specimen are shown diagrammatically in Fig. 17.

¹ The openings in such cloth are of the order of 0.06 mm.

Slits S_1 and S_2 serve to define the X-ray beam. S_3 cuts off any diffraction pattern from the crystals on the edge of S_2 . The specimen of powdered crystal is at C . In the type of apparatus illustrated, the width of the specimen is less than that of the X-ray beam, so that the effective width of the beam is determined by the width of the specimen. The diffraction pattern is recorded on the photographic film P . The filter F renders the rays practically monochromatic. The trap T not only prevents overexposure from the undeviated beam but also, by its shape, prevents fogging the film by rays scattered by the trap from the primary beam. A septum in the film holder allows two diffraction patterns to be taken on the same photographic film.

Ordinarily, if the specimen is a salt or some other brittle type of crystal, it is crushed in an agate mortar. If the specimen is a coarse grained metal, it may be reduced to filings using only light pressure on a very fine, clean file. The powder, or filings, is then sieved through a clean 200-mesh silk bolting cloth. This powder may be mounted in any of several ways. Probably the most common method is to fill it into a thin-walled glass tube of about 0.6 millimeter internal diameter. Care must be taken that the glass contains only elements of low atomic weight. Lead-free lime glass, such as is made for X-ray bulbs by the Vineland Flint Glass Works (Vineland, New Jersey), or pyrex glass tubes, are suitable. They may be drawn down easily from larger-sized tubing. Corning glass, known as 707BM, from the Corning Glass Works (Corning, New York), is especially good. Ordinary hard glass usually contains a little lead and is too opaque to the X-rays. In some cases, celluloid or pyralin tubes may be used to advantage. They are made by the DuPont Viscoloid Co., Arlington, New Jersey.

With little danger of breakage, these tubes may be loaded rapidly by means of the following technique: (1) A plug of cotton is pushed into the tube to a point midway between the ends, using as a ramrod a piece of 10-mil wire of platinum, molybdenum, tungsten, or other non-corrosive material. The plug should not be longer than the width of the septum in the film holder (see Fig. 17). (2) The open end of the tube is scraped along the bowl of the mortar containing the crushed crystal, starting at the bottom and ending at the top (see Fig. 18, *a*, *b*). (3) The tube is then held vertically between the thumb

and index finger of one hand, and the thumb nail is tapped with a pencil. This causes the powder to drop into the tube. (4) These operations are repeated until enough powder has been collected to extend from the septum to a point beyond the edge of the X-ray beam. A second piece of cotton is then inserted to keep the powder in place. (5) The whole procedure is repeated in loading some other crystal into the other half of the specimen-

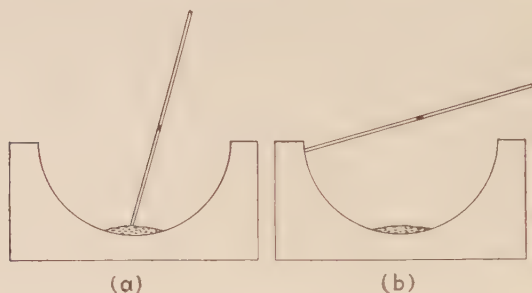


FIG. 18.—Filling a specimen tube. (a) Beginning of stroke. (b) End of stroke.

tube. The first powdered crystal to be loaded is some substance used as a comparison standard, usually sodium chloride ($a = 2.814\text{\AA}$.) which is the secondary standard for interplanar distances.¹ The second substance is the one under investigation. The two ends of the tube are then plugged with sealing wax with the aid of an electrically heated nichrome hairpin, and an

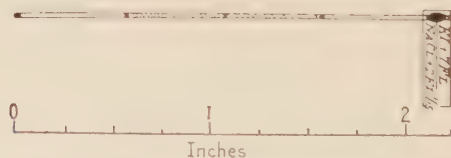


FIG. 19.—Diagram of filled specimen tube.

identification tag is waxed on. Care must be taken that no sealing wax is on that part of the tube exposed to X-rays, for, in such a case, the inorganic filler in the wax will produce a diffraction pattern of its own. If the powdered crystal is slightly hygroscopic, the agate mortar must be kept heated to about 100°C . on a hot plate during the loading operation. A full-size diagram of the loaded tube is shown in Fig. 19.

¹ *Gen. Elec. Rev.*, Vol. XXVII, p. 745, November, 1924.

It is often advisable to anneal the sieved powder. The act of crushing or filing introduces strains into many crystals, thus producing *warped planes* of atoms. The effect of warping on the intensity of the diffracted beam is not very marked for those planes which are farthest apart but becomes quite serious for those planes in the crystal whose interplanar distance is small. Besides reducing the efficiency of diffraction at large angles, warping decreases the resolving power of the crystal fragments. It has already been explained that the nearest convenient approach to monochromatic X-rays gives a beam containing two wave lengths, called α_1 and α_2 , which differ from each other by less than 1 per cent. Each of these is diffracted by the crystal powder independently of the other, so that if the angle of diffraction, θ , is large enough (in the case of Mo rays this is true for an angle of about 21 degrees for a specimen in a cylindrical container about 0.6 millimeter in diameter), each *line* of the diffraction pattern should be a doublet if the crystal is composed of true planes of atoms. If the crystal fragments in the powder have warped planes, each line of these doublets is widened out until the lines of the doublet tend to become merged into a single line of rather hazy outline. The total energy of the diffracted beam from the warped planes is spread out over a larger area of the photographic film, so that the line is less black on the film than it otherwise would be. This gives the effect of a decrease in efficiency of diffraction. This may be illustrated by an experiment with tungsten. A tungsten incandescent lamp was burned for 4 hours at its rated voltage in order to anneal the filament thoroughly. It was then crushed in an agate mortar. A portion of the filament was then

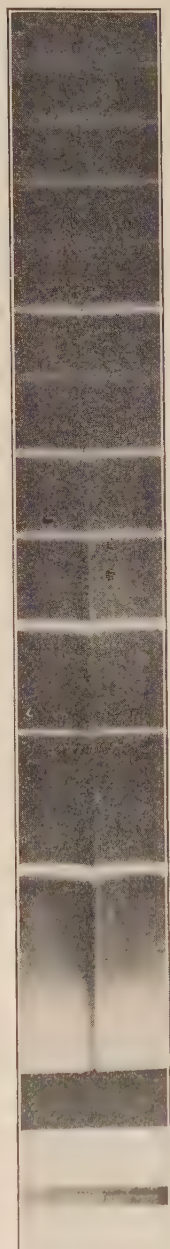


FIG. 20.—Diffraction pattern of strained (above) and unstrained (below) tungsten.

reannealed in hydrogen at the same temperature as before in order to remove the strains produced by crushing. Diffraction patterns of the two portions were taken side by side on the same film. They are shown in Fig. 20.

While the primary beam is traversing the specimen, it suffers absorption. Still further absorption occurs in each of the diffracted beams on its way out from the specimen. If the specimen is mounted as shown in Fig. 17, the optimum thickness of crystalline material is approximately

$$t = \frac{1}{\mu} \quad (2)$$

where μ is the coefficient of absorption of the crystal for the wave length of X-rays used. This may be shown as follows:

If the original intensity of the incident primary beam is I_0 , the intensity after passing through a distance x is reduced to

$$I_1 = I_0 e^{-\mu x}$$

The initial intensity, dI_2 , of a diffracted beam from a layer of thickness dx at a distance x below the surface must be proportional to dx and to I_1 , so that

$$dI_2 = kI_1 dx = kI_0 e^{-\mu x} dx$$

The path of the diffracted beam to the surface of the crystalline material may be expressed approximately as $t - x$, where t is the thickness of the specimen in the direction of the incident beam. The intensity I_3 of the emergent diffracted beam is, therefore, approximately

$$\begin{aligned} I_3 &= \int_0^t kI_0 e^{-\mu x} e^{-\mu(t-x)} dx \\ &= \int_0^t kI_0 e^{-\mu t} dx \\ &= kI_0 t e^{-\mu t} \end{aligned}$$

This will be a maximum if $dI_3/dt = 0$, i.e., when

$$t = \frac{1}{\mu}$$

It is obviously not convenient to use specimen-tubes of different diameter for different crystalline materials. The same effect may be obtained, however, while using tubes of constant diameter, by diluting the powdered crystal with some amorphous material of low opacity to the X-rays. Gum tragacanth is sufficiently amorphous for this purpose. For many crystalline materials the diffraction pattern is so strong in comparison with that from cellulose that cornstarch or flour may be used as a

diluent. In general, the higher the atomic number the greater is the coefficient of absorption of the crystal. For this reason, from the standpoint of Eq. (2), crystals composed of elements of high atomic number should be very greatly diluted. There are, however, practical limits to the amount of dilution, for a point is soon reached where there are in the material not enough crystal fragments which can be packed into a specimen-tube to give a truly chaotic orientation. Figure 21 gives an empirical schedule, used by our own research laboratory, for diluting powdered crystals. At each end of the horizontal rows of Fig.

PERIODIC CLASSIFICATION OF THE ELEMENTS

VOLUME OF DILUTING MATERIAL	GROUP-0	GROUP-1	GROUP-2	GROUP-3	GROUP-4	GROUP-5	GROUP-6	GROUP-7	GROUP-8	VOLUME OF DILUTING MATERIAL
0	HE(2)	H(1)	BE(4)	B(5)	C(6)	N(7)	O(8)	F(9)		0
1	NE(10)	NA(11)	MG(12)	AL(13)	SI(14)	P(15)	S(16)	C(17)		3
4	AI(18)	K(19)	CA(20)	SC(21)	TI(22)	V(23)	CR(24)	MN(25)	FE(26) CO(27) NI(28)	5
5		CU(29)	ZN(30)	GA(31)	GE(32)	AS(33)	SE(34)	BR(35)		6
6	KR(36)	R(37)	SR(38)	Y(39)	ZR(40)	CL(41)	MO(42)	-(43)	RU(44) RH(45) PO(46)	7
7		AG(47)	CD(48)	IN(49)	SN(50)	SB(51)	TE(52)	I(53)		8
8	XE(54)	CS(55)	BA(56)	LA(57)						
9-10			RARE EARTHS							
						TA(73)	W(74)	-(75)	OS(76) IR(77) PT(78)	12
12-15	NT(86)	AU(79) -(87)	HG(80) ACX(88) THX FA MTH	TL(81) AC(89) MTH ₂	PB(82) ROAC(90) RTH IO TH UX ₁	BR(83) UX ₂ (91)	PO(84) U ₁ (92) U ₂	(95) -		

FIG. 21.—Empirical dilutions of powdered material.

21 will be found a number. This represents the number of volumes of diluting material to be mixed with one volume of an element at that end of the row. If the crystal is a compound, the weighted average is taken of the dilutions for the elements in the compound, the weights being proportional to the number of atoms of the element in the chemical formula for the compound.

In certain cases, the glass specimen-tube may be dispensed with. If the specimen is not hygroscopic and is not readily oxidized in the air, the powdered crystal may be mixed with an amorphous adhesive, such as gum tragacanth and pressed up into a thin slab. This slab may then be used directly with the second type of slit (0.02- by 0.50-inch opening). If the slab has a thin, flat edge, it may be used with the first type of slit (0.06- by 0.50-inch opening). In this case, it must be mounted with its edge at C (Fig. 22), so as to make a very slight angle with the primary beam. The edges of the lines in the diffraction pattern are

sharpened if some opaque, amorphous material such as lead glass is used as a backing. In some cases, it is possible to substitute for the slab and lead glass a strip of thin cardboard which has a layer of the powder stuck on its edge. The crystals of mechanically worked metals are usually very small. If the specimen to be examined is a thin sheet of metal having a straight edge, it may be mounted in the same manner as the slab described above when the wide slits are used. Most metals are sufficiently opaque to the X-rays used in crystal analysis so that the lead glass *backing* is unnecessary. If the metal is in the form of a thin wire, it may be stretched out in the path of the beam, so as to

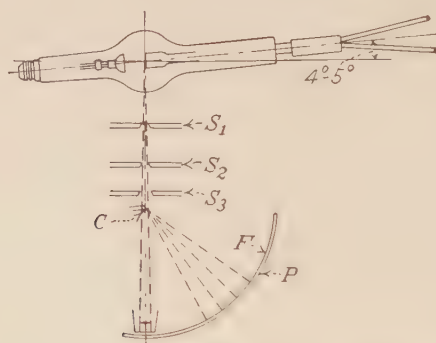


FIG. 22.—Powder method applied to a pressed block.

take the place of the specimen-tube of Fig. 17. This is one of the most desirable methods of mounting a specimen when no other diffraction pattern is to be taken on the same film for purposes of comparison. If a comparison pattern is desired, the wire and the comparison standard may be mounted along the same straight line on the edge of an amorphous holder, such as a slab of pressed gum tragacanth or a sheet of glass, or the wire and the comparison standard may be inserted in opposite ends of a glass or celluloid specimen-tube. If the wire is of very fine diameter, it is best to use several lengths side by side. For 5-mil tungsten wire, six or seven lengths are sufficient. If the specimen is in the form of a metal foil, it may be mounted in sheet form in front of one of the long, narrow slits.

The Diffraction Pattern and Its Interpretation in Terms of Space Lattices.—It is inherent in the powder method that all the families of atomic planes in the specimen send out their diffracted beam simultaneously. A single photographic film may,

therefore, be made to record the whole diffraction pattern or as much of it as may be desired. Each family of planes in the powdered crystal produces a line on the film for its first-order diffracted beam and additional lines for such other orders of diffraction as may be physically possible, provided only that $n\lambda/2d$ is less than unity (see Eq. (1)). The photographic record of the diffraction pattern is, therefore, a series of lines whose angular distances from the *zero line* (photographic record of the undeviated beam) are characteristic of the various interplanar spacings in the crystal. From these angular distances and the wave length of the X-rays, the interplanar spacings may be calculated at once from Eq. (1) or may be read off directly from the scale of Fig. 16.

Knowing the interplanar spacings, it is possible, at least in the case of the simpler crystal systems, to find, by systematic cut-and-try methods, an arrangement of atoms in space which will account for the observed interplanar distances. The situation may be visualized by the following illustrations in two dimensions:

If the trees of an orchard are planted according to some systematic geometrical scheme, they will appear to be in rows whose direction and distance apart will depend upon the position of the observer with respect to the orchard. Now, suppose that the reader had never seen the orchard but had been supplied with data giving the distance apart of these various rows of trees, and suppose that it is required to draw a map to scale showing the positions of the trees in the orchard. It would be necessary to list the data in a column in the order of the size of the numbers, starting with the largest number at the top of the column. In a parallel column, a corresponding list would be made of the ratios of the several distances to the largest distance, as in Table I. Some geometrical configuration of trees must now be assumed, and the ratios of distances required by that configuration must be compared with the tabulated ratios. If they do not agree, a new configuration must be assumed and its ratios compared with those listed from the data. The data of Table I are from an orchard set out so that the trees are at the corners of imaginary squares, for such a configuration gives ratios of 1, $1/\sqrt{2}$, $1/\sqrt{5}$, $1/\sqrt{10}$, $1/\sqrt{13}$, $1/\sqrt{17}$, etc., which are identical with the ratios of the tabulated data. It is evident that the side of the imaginary unit square is 25 feet long.

TABLE I.—DISTANCE BETWEEN ROWS IN A SIMPLE-SQUARE (TWO-DIMENSIONAL) LATTICE

Distance between rows, feet	Ratio from experiment (25.0 = 1)	Ratio calculated for simple square	Miller indices for rows of simple square
25.0	1.00	1.00	1, 0
17.7	0.71	0.707	1, 1
11.2	0.45	0.447	2, 1
7.9	0.32	0.316	3, 1
6.9	0.28	0.277	3, 2
6.0	0.24	0.242	4, 1

Suppose the distances between rows had been those listed in the first column of Table II. Certain of the ratios in the second column are identical with those of Table I. Such an accidental agreement cannot be taken to mean that the plan of the orchard of Table II is a simple square, for if every experimental ratio is

TABLE II.—DISTANCE BETWEEN ROWS IN A CENTERED-SQUARE (TWO-DIMENSIONAL) LATTICE

Distances between rows, feet	Ratio from experiment 17.7 = 1.00	Ratio calculated for centered square	Ratio from experiment 25.0 = 1.00	Ratio calculated for centered square	Miller indices for rows of centered square
17.7	1.00	1.00	0.71	0.707	1, 1
12.5	0.71	0.707	0.50	0.500	1, 0
7.9	0.45	0.447	0.32	0.316	3, 1
5.6	0.32	0.316	0.22	0.223	2, 1
3.4	0.19	0.195	0.14	0.138	3, 2
3.0	0.17	0.171	0.12	0.121	4, 1

not duplicated within the precision of the data in the table of calculated ratios, the solution cannot be valid. Trials show that every experimental ratio is duplicated in the ratios calculated for a centered square. In this configuration, some of the trees are at the corners of imaginary squares and additional trees are at the centers of these squares, so that the configuration is that of the figure five on dice. The actual distances in Table II may be accounted for if the side of the unit square is 25 feet long. If the side of the square is taken as the unit of measure,

the experimental distances give the ratios listed in the fourth column. The corresponding calculated ratios are given in the fifth column. A comparison of the fifth column of Table II with the third column of Table I shows that the effect of the additional trees has not been to produce rows in new directions in the orchard but only to cut in half the distances between those rows which have one even Miller index.¹

The interpretation in terms of space lattices of the diffraction pattern of a powdered crystal is much like the foregoing illustration, except that there are three dimensions to be considered instead of two and the data include fictitious distances d/n caused by lines in the diffraction pattern corresponding to the second, third, etc., orders of diffraction. In the cubic system, it is easy to make reference tables, such as Table III of interplanar distances, taking the side of the unit cube as the unit of length. The fictitious distances representing second-order diffraction are listed in the table as if they actually existed, so that the table corresponds to all the interplanar distances calculated from the diffraction pattern just as truly as Tables I and II correspond to all the distances measured in the orchards. An inspection of Table III shows that the pattern for a simple cubic crystal contains every possible line which can be produced by a crystal having cubic symmetry. When the crystal structure is made more complicated by placing additional atoms in symmetrical positions in the simple cube without changing the dimensions of the cube, the effect is not to add more lines but to wipe out certain lines from the simple cubic pattern. This is brought out in Fig. 23, which is plotted from Table III. The actual diffraction patterns differ from those of Fig. 23 in that they include the sine law of Eq. (1).

Each spacing for a simple cubic lattice is the reciprocal of the square root of the sum of three squares. These spacings, therefore, decrease in regular fashion for the first six lines of the diffraction pattern. There is, however, no line corresponding to $1/\sqrt{7}$, for no three squares can add up to seven. Similar breaks may be found at $1/\sqrt{15}$, $1/\sqrt{23}$, $1/\sqrt{28}$, etc. If, therefore, a diffraction pattern is found to have six lines regularly spaced,

¹ Miller indices are the reciprocals of the intercepts of the line on the X- and Y-axes. In the case of a plane of atoms in a crystal, the Miller indices are the reciprocals of the intercepts of the plane on the X-, Y-, and Z-axes.

TABLE III.—INTERPLANAR SPACINGS IN TYPICAL CUBIC CRYSTALS

Miller indices, h, k, l	$h^2 + k^2 + l^2$	Number of families of planes	Interplanar spacings, including the fictitious spacings for various orders of diffraction, $n = 2, n = 3, \dots$			
			Simple cube	Body-centered cube	Face-centered cube	Diamond cube
100	1	3	1.000			
110	2	6	0.7071	0.7071		
111	3	4	0.5770	0.5770	0.5770
100	4	3 ($n = 2$)	0.5000	0.5000	0.5000	
210	5	12	0.4472			
211	6	12	0.4083	0.4083		
110	8	6 ($n = 2$)	0.3536	($n = 2$) 0.3536	0.3536	0.3536
221	9	12	0.3333			
100	9	3 ($n = 3$)	0.3333			
310	10	12	0.3160	0.3160		
311	11	12	0.3014	0.3014	0.3014
111	12	4 ($n = 2$)	0.2885	0.2885	($n = 2$) 0.2885	
320	13	12	0.2774			
321	14	24	0.2672	0.2672		
100	16	3 ($n = 4$)	0.2500	($n = 2$) 0.2500	($n = 2$) 0.2500	0.2500
410	17	12	0.2423			
322	17	12	0.2423			
411	18	12	0.2358	0.2358		
110	18	6 ($n = 3$)	0.2358	($n = 3$) 0.2358		
331	19	12	0.2292	0.2292	0.2292
210	20	12 ($n = 2$)	0.2234	0.2234	0.2234	
421	21	24	0.2180			
332	22	12	0.2132	0.2132		
211	24	12 ($n = 2$)	0.2040	($n = 2$) 0.2040	0.2040	0.2040
430	25	12	0.2000			
100	25	3 ($n = 5$)	0.2000			
431	26	24	0.1960	0.1960		
510	26	12	0.1960	0.1960		
511	27	12	0.1923		0.1923	0.1923
111	27	4 ($n = 3$)	0.1923	($n = 3$) 0.1923	($n = 3$) 0.1923
520	29	12	0.1856			
432	29	24	0.1856			
521	30	24	0.1826	0.1826		
110	32	6 ($n = 4$)	0.1766	($n = 4$) 0.1766	($n = 2$) 0.1766	($n = 2$) 0.1766
530	33	12	0.1714		
433	33	12	0.1714		
531	34	24	0.1693	0.1693
100	36	3	($n = 3$) 0.1667	($n = 3$) 0.1667	
221	36	12	0.1667	0.1667	
611	36	12	0.1621		
532	36	24	0.1621		
310	36	12	($n = 2$) 0.1580	0.1580	0.1580
533	39	12	0.1525	0.1525
311	39	12	0.1507	($n = 2$) 0.1507	
631	42	24	0.1474		
111	44	4	($n = 2$) 0.1442	($n = 4$) 0.1442	($n = 4$) 0.1442
110	44	6	($n = 5$) 0.1414		
710	44	12	0.1414		
543	44	24	0.1414		

TABLE III.—INTERPLANAR SPACINGS IN TYPICAL CUBIC CRYSTALS.—
(Continued)

Miller ¹ indices, h, k, l	$h^2 + k^2 + l^2$	Number of families of planes	Interplanar spacings, including the fictitious spacings for various orders of diffraction, $n = 2, n = 3, \dots$			
			Simple cube	Body-centered cube	Face-centered cube	Diamond cube
711 } 551 } 320 } 211 } 552 } 721 } 321 } 730 } 553 } 731 } 732 } 651 } 100 } 741 } 811 } 554 } 733 } 410 } 322 }	12 } 12 } 12 } 12 } 12 } 24 } 24 } 12 } 12 } 24 } 24 } 24 } 3 } 24 } 12 } 12 } 12 } 12 } 0.1387 0.1400 0.1400 0.1387 0.1336 0.1301 0.1301 0.1250 0.1230 0.1230 0.1222 0.1212 0.1212 0.1400 0.1400 0.1336 0.1301 0.1301 0.1250 0.1222

followed by a vacant place where the seventh line might be expected, it should be tested quantitatively at once to see if the ratios of spacings correspond to those of a simple cubic lattice. The spacings for the first six planes of a body-centered cubic lat-



FIG. 23.—Effect of diffraction pattern of complicating the crystal structure.

tice decrease in a regular way as do those of a simple cubic lattice. In fact, if, in Table III, instead of using as a unit of measure the width of the unit cube, we had used the largest interplanar spacing calculated from the diffraction pattern (the 1 1 0 planes), we should have found exactly the same ratios as in the simple

cubic lattice. The diffraction pattern of a body-centered cubic lattice differs markedly, however, from that of a simple cubic lattice, in that there is no break in the regularity of spacing of the lines until after the thirteenth line. The diffraction pattern of a face-centered cubic lattice has the first nine lines grouped so as to form three repetitions of a *pair followed by a single line*. The tenth line, corresponding to the spacing $1/\sqrt{26}$, would be the first line of the next pair except that the second line of the pair would correspond to a spacing $1/\sqrt{28}$, which cannot exist. The sequence of *pair and one* is continued for three more groups, after which it is broken up again by missing lines. The diffraction pattern of a diamond cubic lattice consists of a single line followed by succession of pairs.

Graphical Methods of Interpretation.—The quantitative examination of the diffraction pattern of a cubic crystal in terms of space lattices is most easily made with the aid of a slide rule. If the slide of the slide rule is turned so that the numbers are

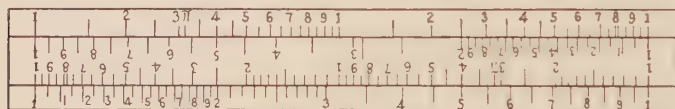


FIG. 24.—Slide rule arranged for quantitative study of diffraction patterns of cubic crystals.

upside down and the ends of the scales are made to register with each other (Fig. 24), it will be found that readings on the lower scale of the body of the slide rule are opposite the reciprocals of their squares on the inverted slide. If the slide is pushed along, any two readings on the lower scale of the body of the rule have the same ratio as the reciprocals of the square roots of the corresponding readings on the lower (adjacent) scale of the inverted slide. The interplanar distances of a crystal, as calculated from the diffraction pattern with the aid of Eq. (1), are, therefore, plotted on the lower scale of the body of the slide rule, using a soft lead pencil. The interplanar distances usually measured from the diffraction pattern range for most crystals from 2 or 3\AA . down to about 0.6 to 0.7\AA . At 1.00\AA ., the plot runs off the left-hand edge of the scale and must be continued at the right-hand end. The inverted slide is pushed along until 1 is opposite the pencil mark corresponding to the greatest interplanar distance. Suppose

that the next pencil mark is found opposite 2, the next opposite 3, etc. Taking note of the reading on the slide which is opposite 1.00 at the left-hand end of the fixed scale, move the slide back until this reading is opposite 1.00 at the right-hand end of the fixed scale (see Fig. 25). If all the remaining pencil marks also come opposite integers on the slide, the crystal is built on a simple cubic lattice, for its interplanar distances have the same ratios as those listed in the fourth column of Table III. If an exact match is not obtained, the slide is moved back until 2 on the inverted slide is opposite the pencil mark corresponding to the greatest interplanar distance. Then, if all the pencil marks are opposite even numbers on the inverted slide, the crystal is body-centered cubic. If an exact match is still not found, the slide is moved back until 3 on the inverted slide is opposite the first pencil mark, and the pattern, as plotted out on the body of the rule, is examined to see whether every pencil mark is opposite an integer on the inverted slide. If so, a comparison with the ratios of Table III will show whether the diffraction pattern is characteristic of a face-centered or of a diamond cube. A similar procedure may be employed for still other types of cubic crystals. In all cases, if an exact match is obtained within the limits set by the accuracy of the data, the reading on the lower scale of the body of the slide rule opposite 1 on the slide is the length in Ångström units (10^{-8} centimeters) of the edge of the unit cube. It is important that the match be exact within



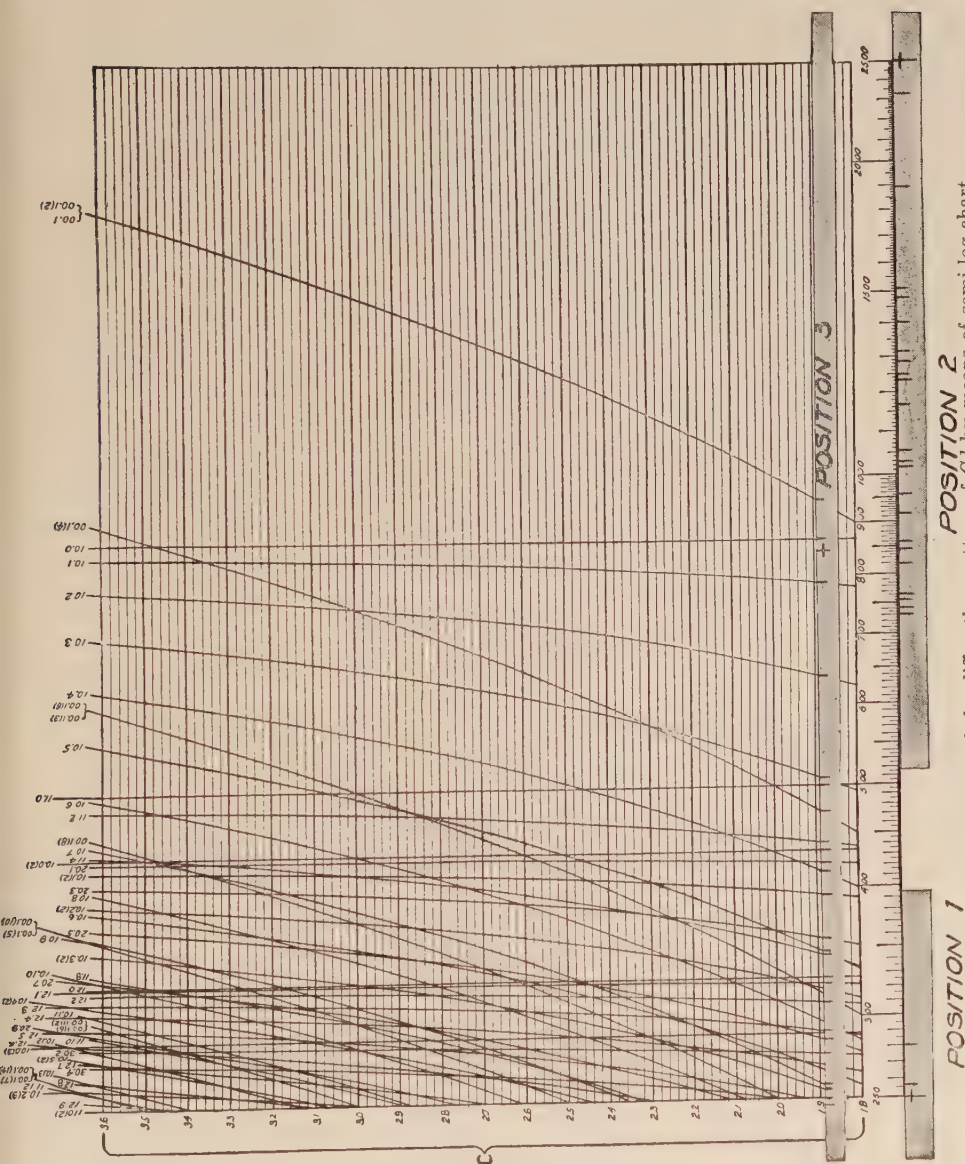
FIG. 25.—Slide rule marked with a body-centered diffraction pattern. (a) Slide at left-hand end. (b) Slide at right-hand end.

the precision of the experimental data. If any lines in the experimental diffraction pattern are unaccounted for, either the solution is invalid, or it must be shown that the specimen consists of a mechanical mixture of two crystals such that every line is accounted for.

The usefulness of the slide rule in the solution of diffraction patterns of cubic crystals is due to the fact that the distances engraved on it are proportional to the logarithms of the numbers rather than to the numbers themselves. Since the scale on the body of the slide rule on which the experimental interplanar distances are plotted is also logarithmic, a direct comparison can be made between the two sets of ratios without further reference to the absolute values of the interplanar distances. This principle was used by the writer in developing a series of semilogarithmic charts for the rapid solution of the diffraction patterns of crystals belonging to the tetragonal and hexagonal systems. The logarithms of the interplanar spacings d were plotted as functions of the axial ratio C . For any given value of C , the lines of the chart have the same relation to the theoretical ratios of distances in the tetragonal or hexagonal systems of crystals that the readings on the inverted slide of the slide rule had for the cubic system. The experimental data are plotted to the same logarithmic scale on the edge of a piece of paper, and this plot corresponds to the pencil-mark plot on the lower scale of the body of the slide rule. Such charts were made and published¹ for the simple, body-centered, and face-centered tetragonal lattices and for the simple-triangular, triangular close-packed, and rhombohedral lattices. Although the diffraction pattern was plotted as $\log d$, the scale of abscissas was shown in terms of d itself, just as on a slide rule, in order to facilitate the work of plotting the pattern. Figure 26 illustrates the use of a chart of this sort in the interpretation of experimental data on cadmium.

This method of interpretation is also applicable to diffraction patterns of crystals belonging to the orthorhombic system. A series of charts would be needed, each chart showing the dependence of the interplanar distance, upon one of the axial ratios C , while the other axial ratio A is kept constant. The whole series of charts would have to cover a range of successive values of A . The ranges from $A = 0.90$ to $A = 1.10$ and $A = 1.50$ to $A = 1.90$ are probably the most important. If the charts

¹ These charts are reproduced as Fig. 27.



were limited to values of C lying between $C = 0.50$ and $C = 1.80$, each chart would require an average of 700 calculations. The ranges for A given above would require 60 such charts for the simple orthorhombic lattice alone. Eight such charts have been prepared by J. O. Wilhelm¹ covering the range from $a:b:c = a:1:0.8$ to $a:b:c = a:1:1.5$. They are reproduced here as Fig. 28 with his permission. The method is hardly applicable to diffraction patterns of monoclinic and triclinic crystals. Of course, if the axial ratios and angles are known for some given substance from ordinary crystallographic measurements, the theoretical interplanar distances may be calculated at once, plotted on the inverted side of a slide rule, and compared with the experimental pattern plotted on the bottom scale of the rule. Then, a consideration of what lines, if any, are missing may give a clue to the degree of complexity of the inner structure of the unit crystal.

After an exact match is found for the experimental pattern, it should be verified by computing the density of the specimen in the following manner:

1. If the match is in the cubic system, the density of the substance is given by

$$\rho = n \frac{M \times 1.649 \times 10^{-24}}{(a \times 10^{-8})^3}$$

where

ρ is the density,

M is the molecular weight of the substance,

1.649×10^{-24} is the mass in grams of one unit of molecular (or atomic) weight.

a is the side of the elementary cube (it is the distance in Ångströms between the 1:0:0 planes in the crystal)

n is the number of points associated with a unit cube in the crystal lattice; n is

1 for the simple cubic lattice,

2 for the body-centered cubic lattice,

4 for the face-centered cubic lattice,

8 for the diamond-cube lattice.

If the line corresponding to the "1 0 0 planes" is absent (as in the case of the body-centered and diamond divisions) then twice the distance corresponding to the second-order line,

¹ McLENNAN and WILHELM, *Phil. Mag.* **3**, 383 (1927).

called in the plots "1 0 0 (2)—1 0 0," must be used as the side of the elementary cube.

2. If the match is found in the tetragonal system, the density is obviously

$$\rho = n \frac{M \times 1.649 \times 10^{-24}}{c(a \times 10^{-8})^3}$$

where c is the axial ratio and n has the same values as before.

3. If the match is found in the hexagonal system, find the distance corresponding to the 1 0 0 planes. (If the match is found in the rhombohedral division, three times the distance corresponding to the third-order line, called in the plots

$\left\{ \begin{array}{l} 1 \ 0 \ 0 \ (1) \\ 1 \ 0 \ 0 \ (3) \end{array} \right\}$, must be used.) This is the altitude of the equi-

lateral triangle which forms the base of the unit prism. The side a of the unit triangle is $2/\sqrt{3}$ times this distance. The density of the specimen is, therefore,

$$\rho = n \frac{M \times 1.649 \times 10^{-24}}{\sqrt{3/4}c(a \times 10^{-8})^3}$$

where

a is the side of the unit triangle,

n is $\frac{1}{2}$ for a simple triangular lattice,

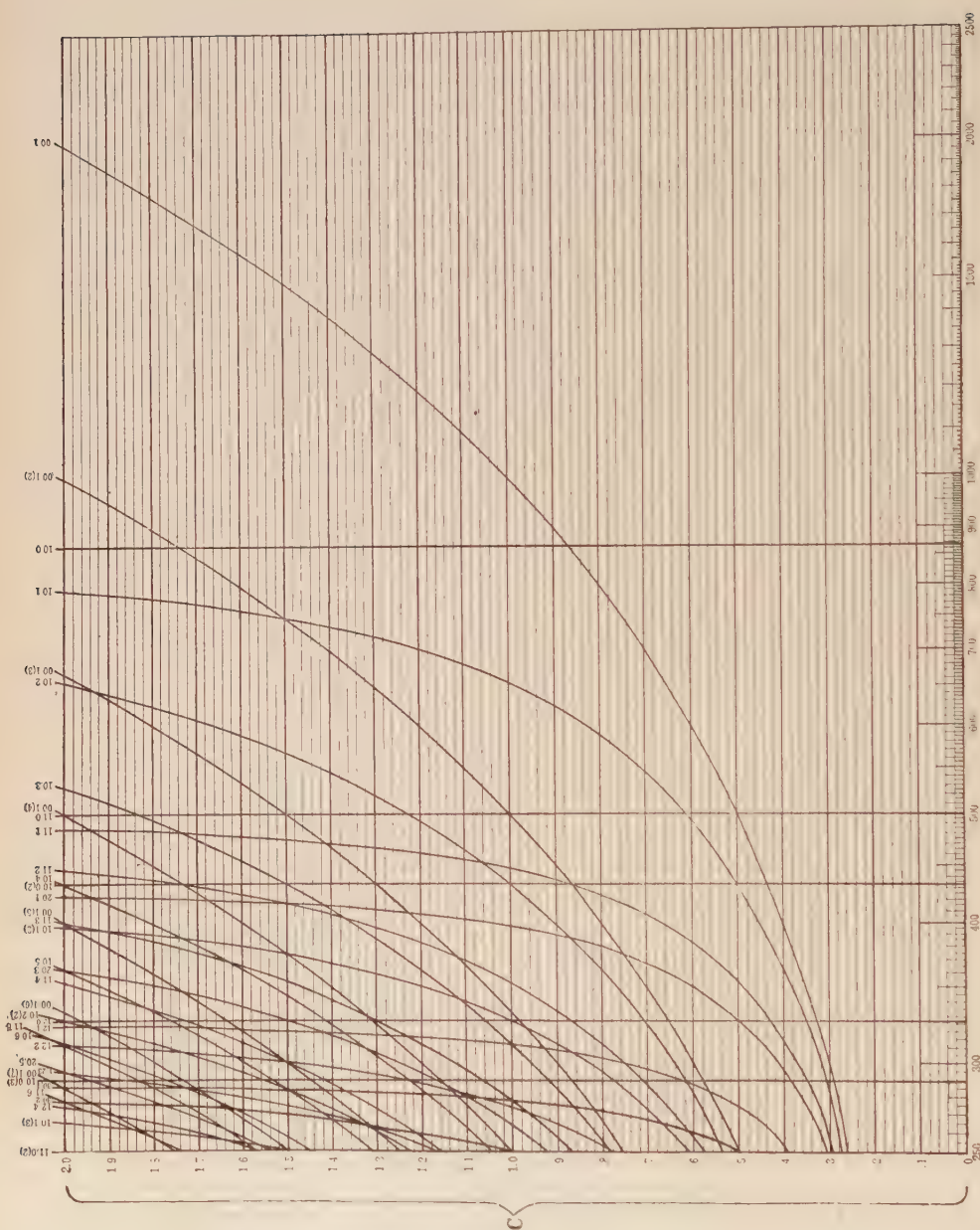
1 for a triangular close-packed lattice,

$\frac{1}{2}$ for a rhombohedral lattice.

A complete analysis of crystal structure will usually require in addition to the above, the application of the Theory of Space Groups. A discussion of this would be beyond the scope of this chapter.

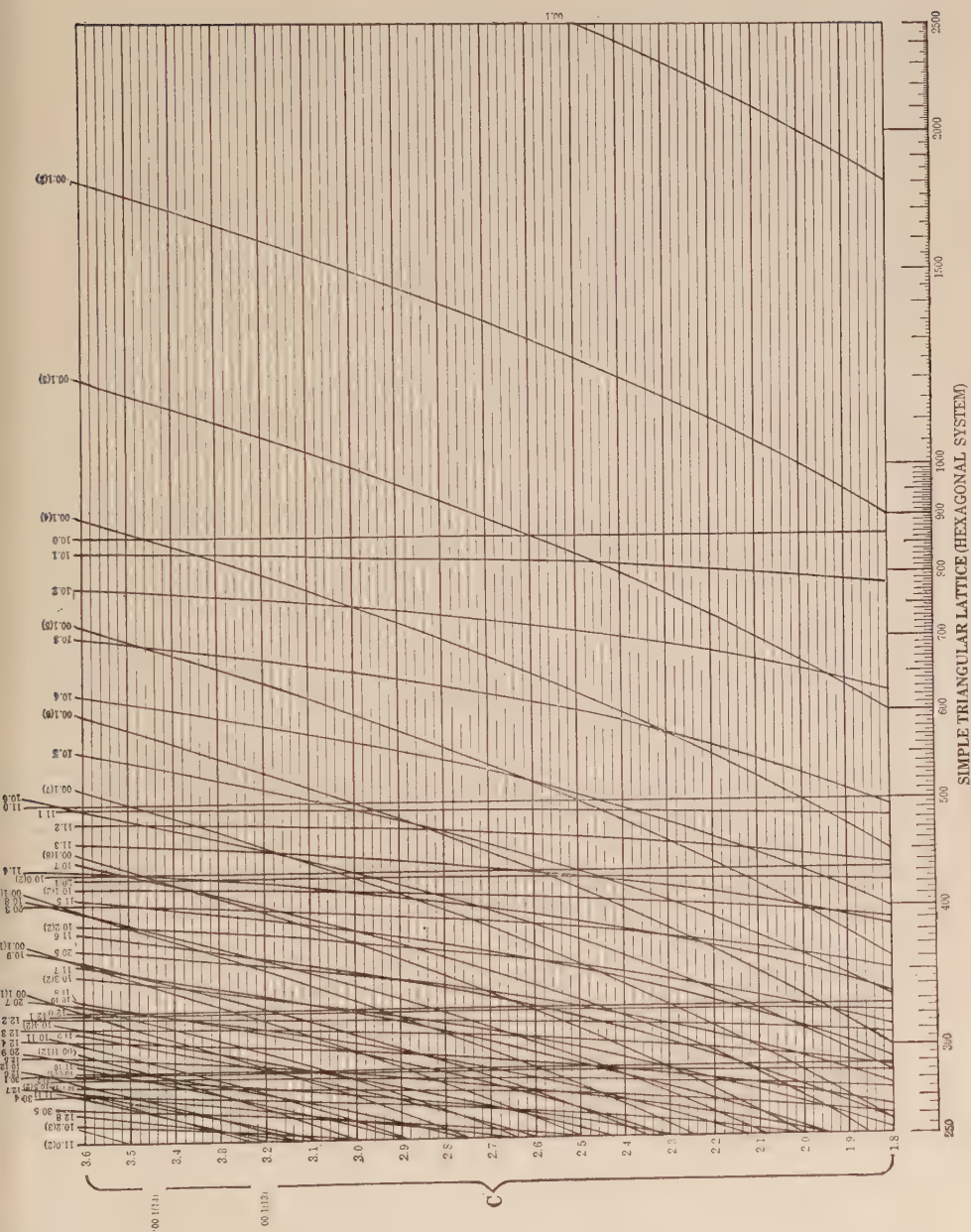
Number of Lines Required.—No matter what method is used for the interpretation of diffraction patterns, too much emphasis cannot be placed upon the necessity for having a sufficiently large number of lines in the diffraction pattern. It has already been shown that the ratios between the interplanar distances for the first six lines of a simple cubic pattern are the same as for a body-centered cubic pattern. Many other instances will be found from the semilog charts of Figs. 27 and 28, where the first few lines are often identical for widely different crystal structures. Such diffraction patterns can be differentiated from each other only when lines are present in sufficient number.

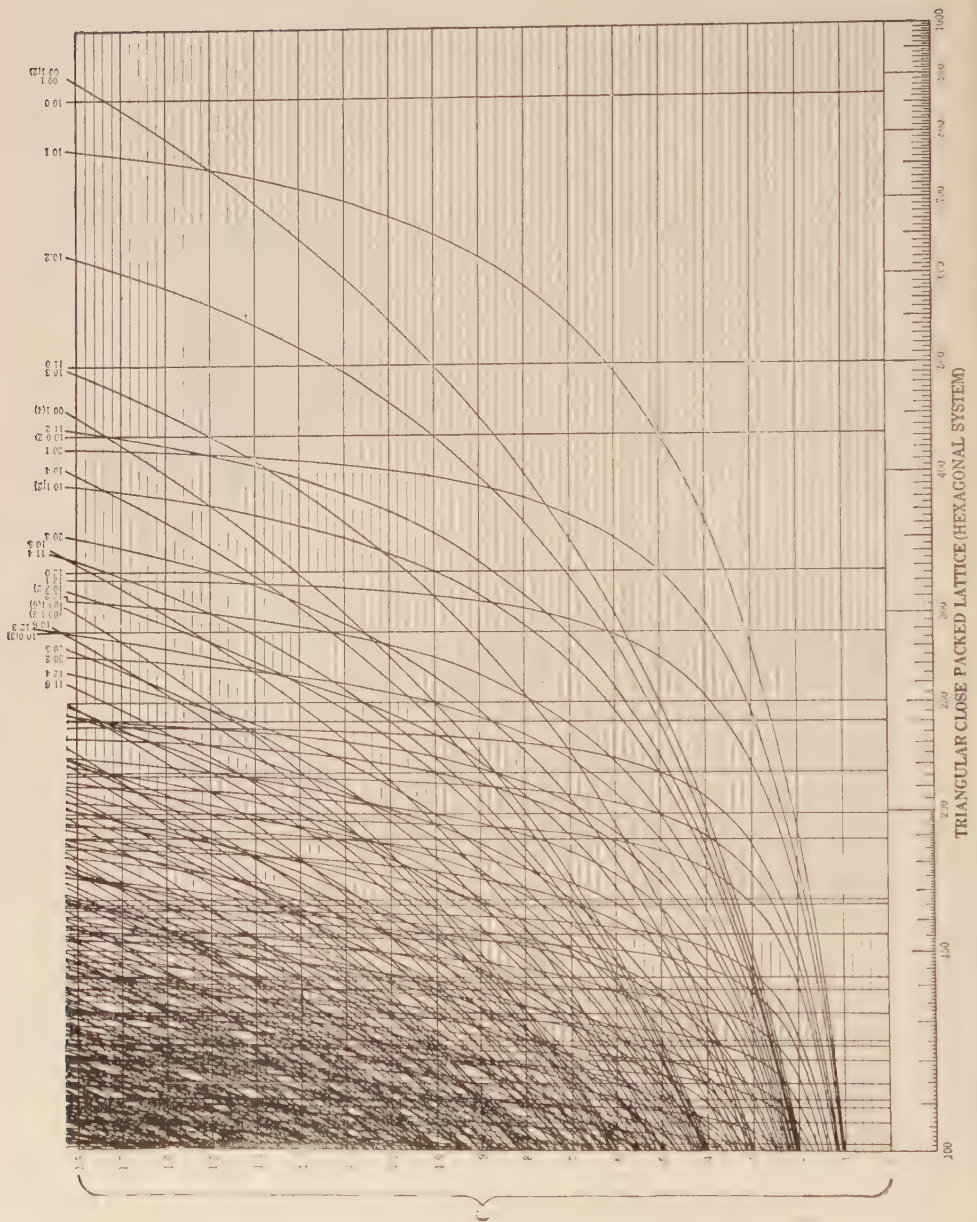
In most cases, the diffraction pattern should be investigated through an angle corresponding to an interplanar distance of



SIMPLE TRIANGULAR LATTICE (HEXAGONAL SYSTEM)

FIG. 27 a.





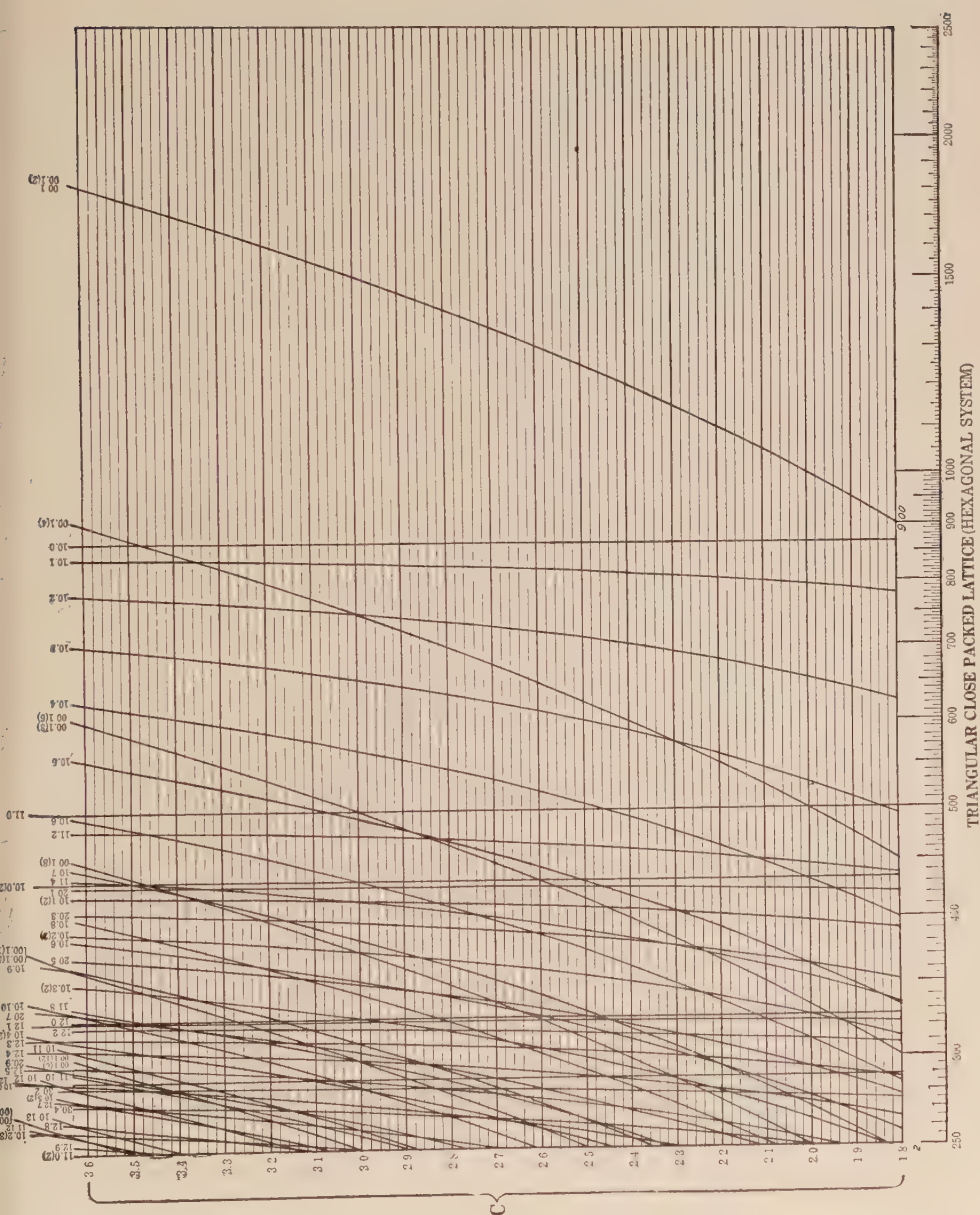
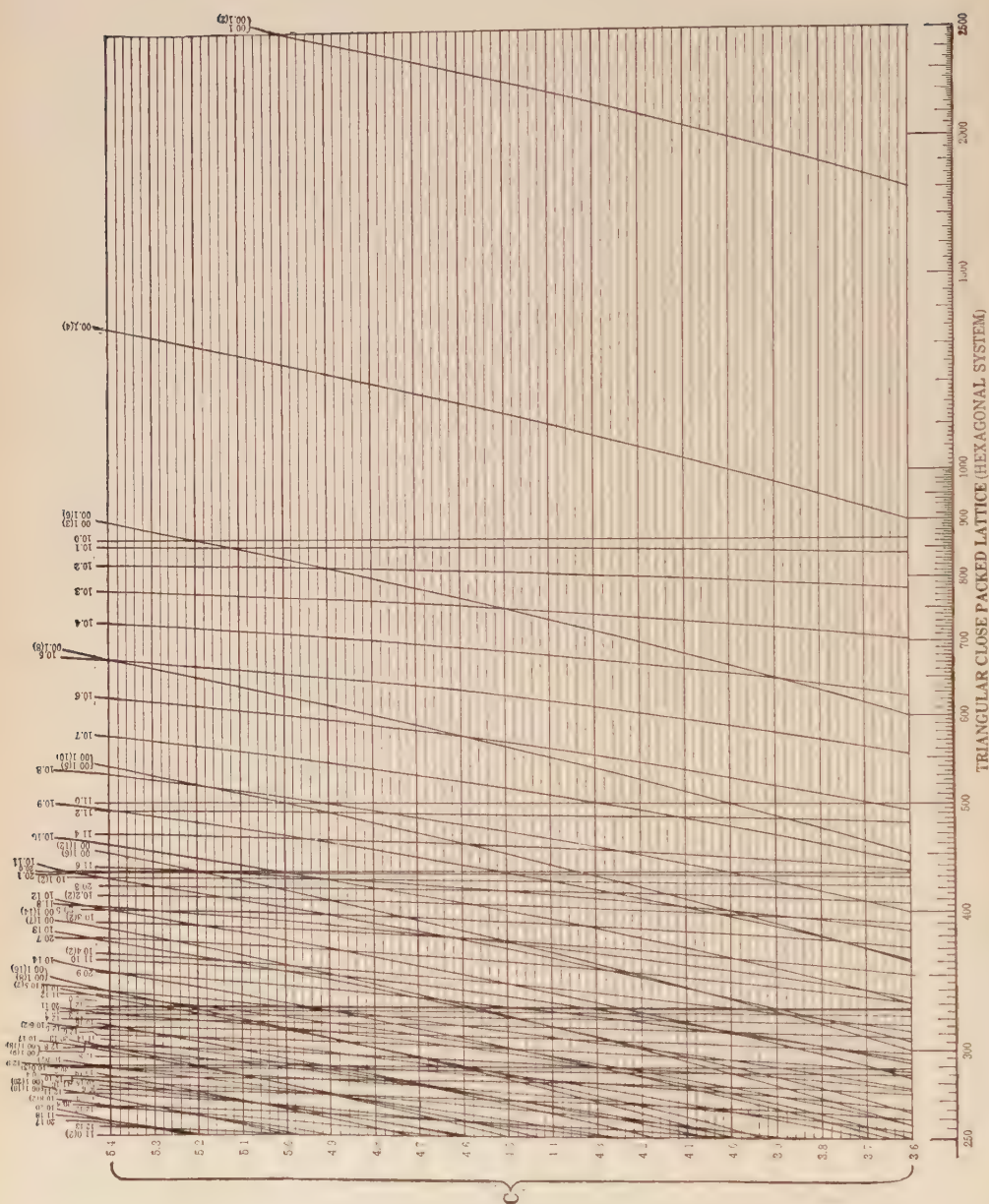
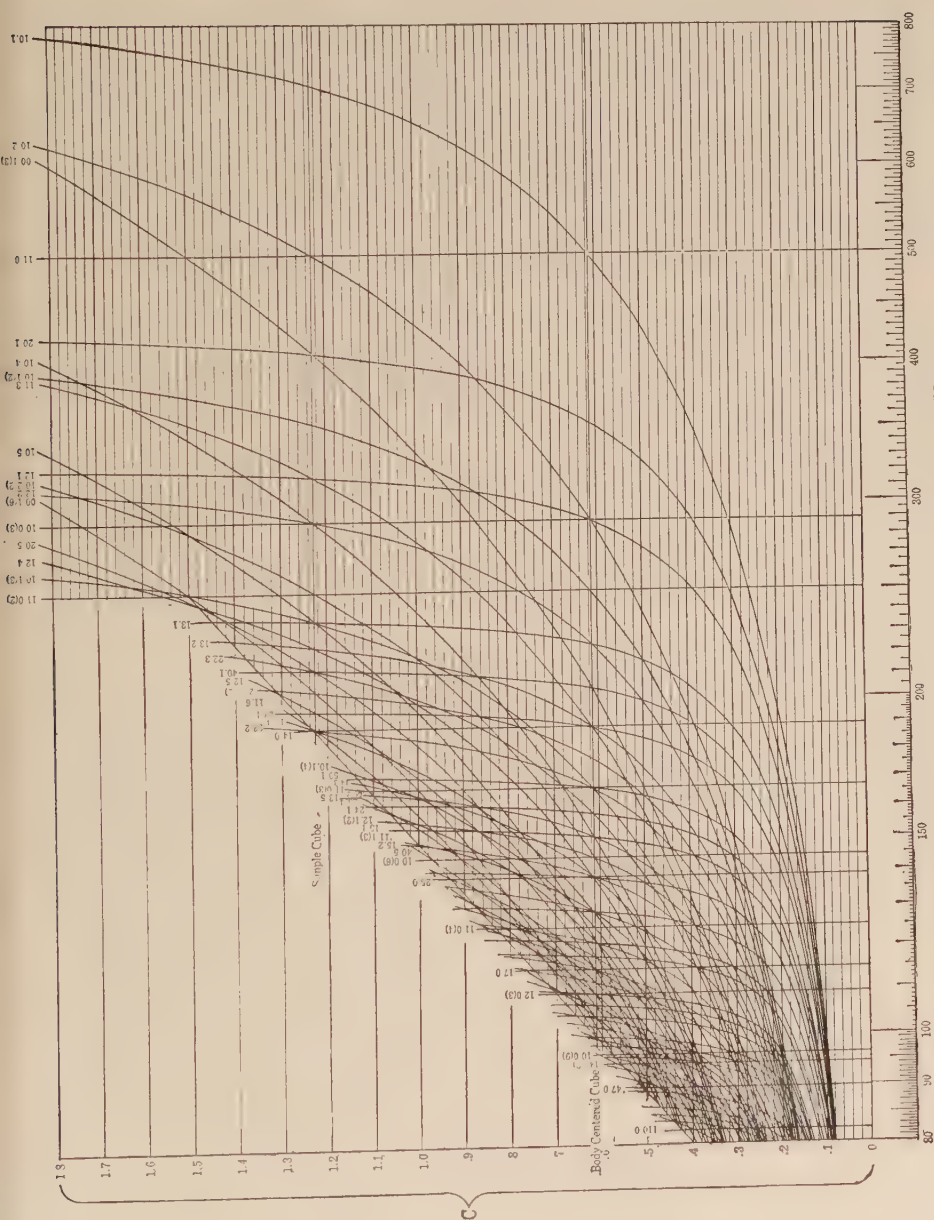
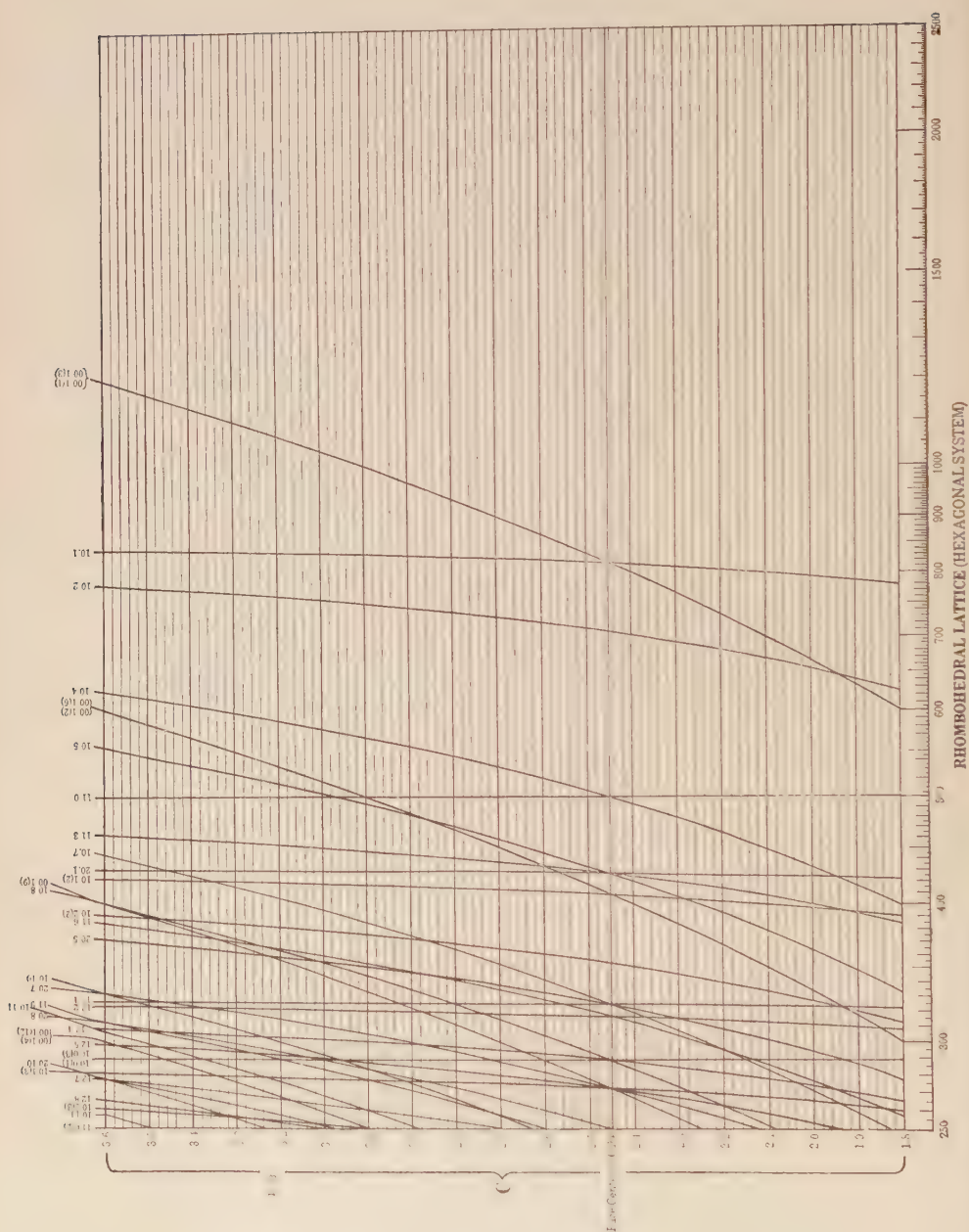
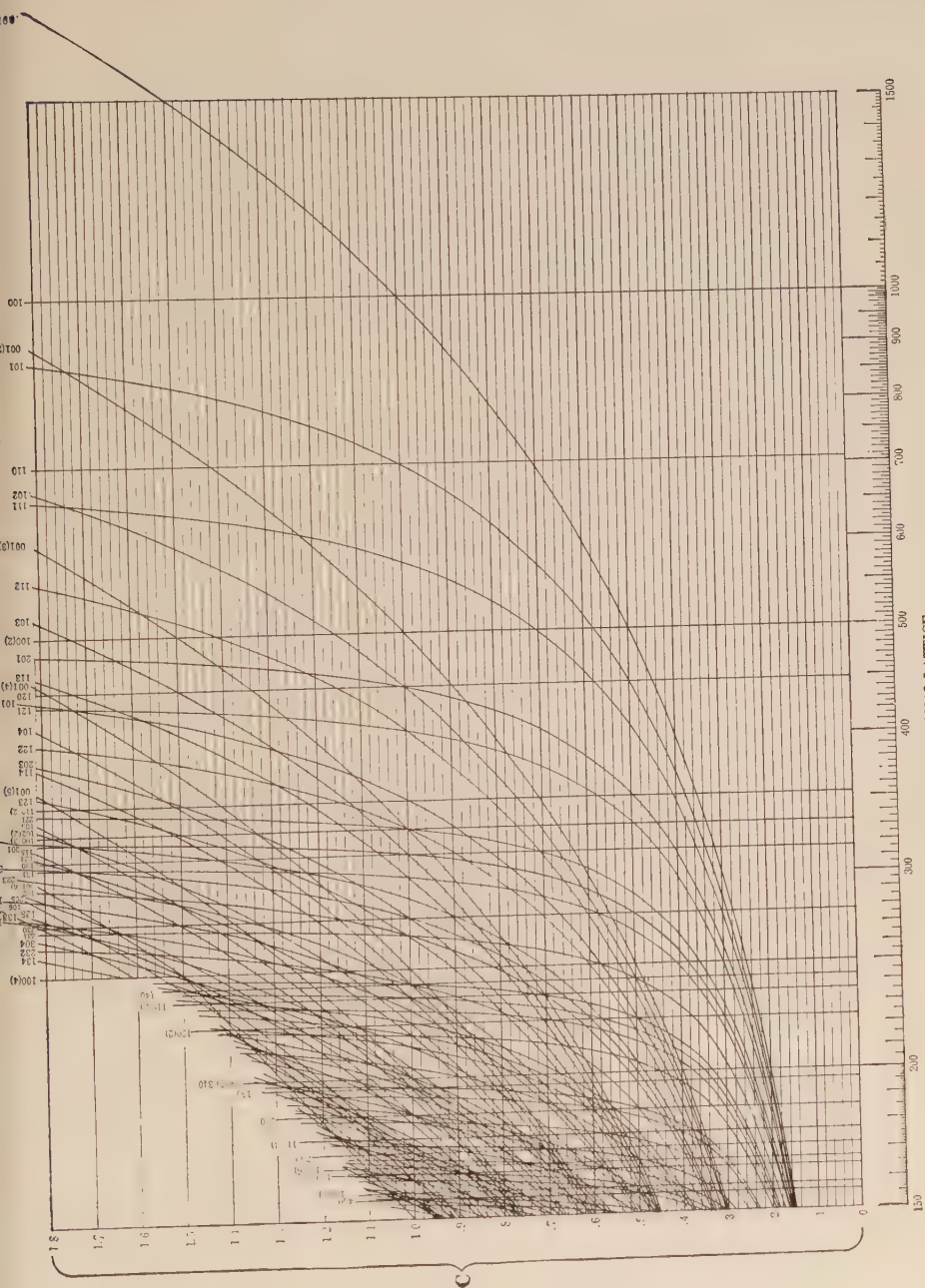


FIG. 27d.



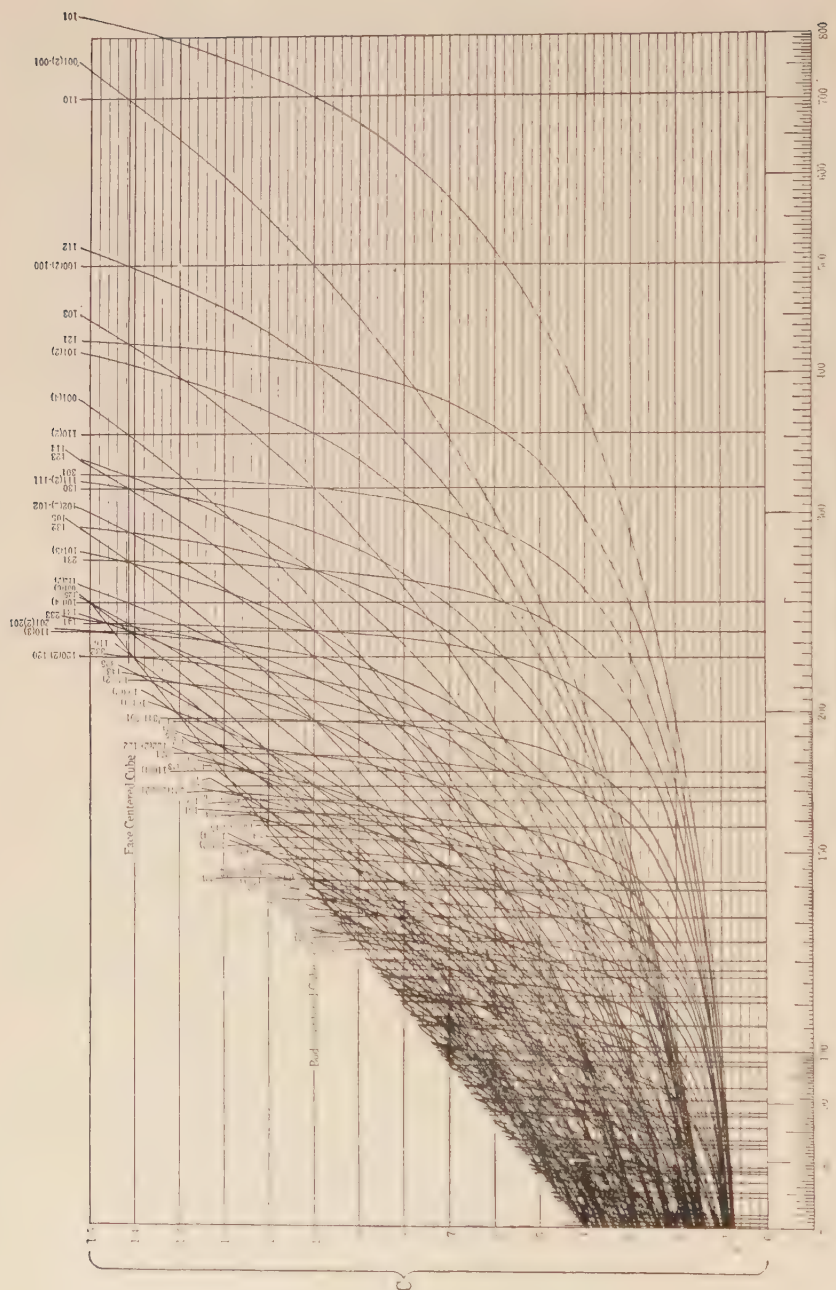


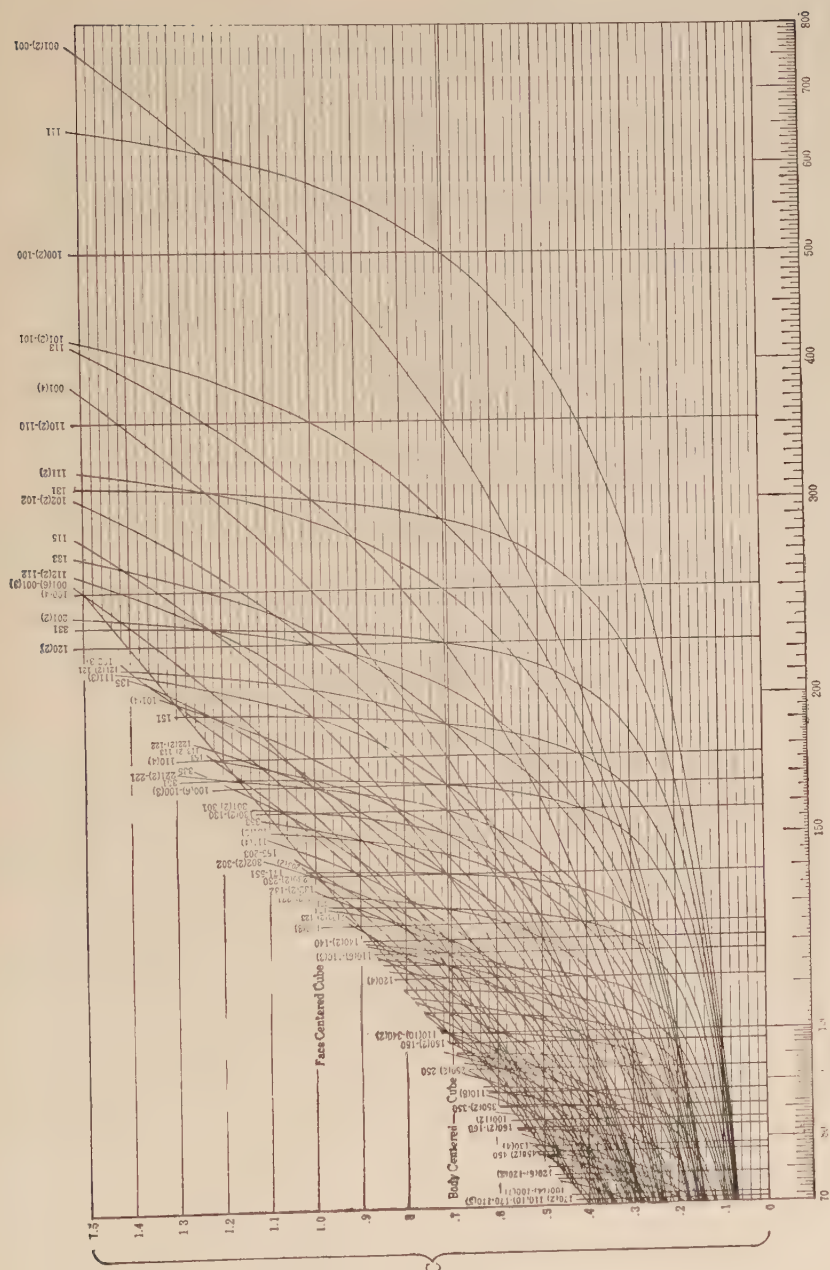




SIMPLE TETRAGONAL LATTICE

Fig. 27h.





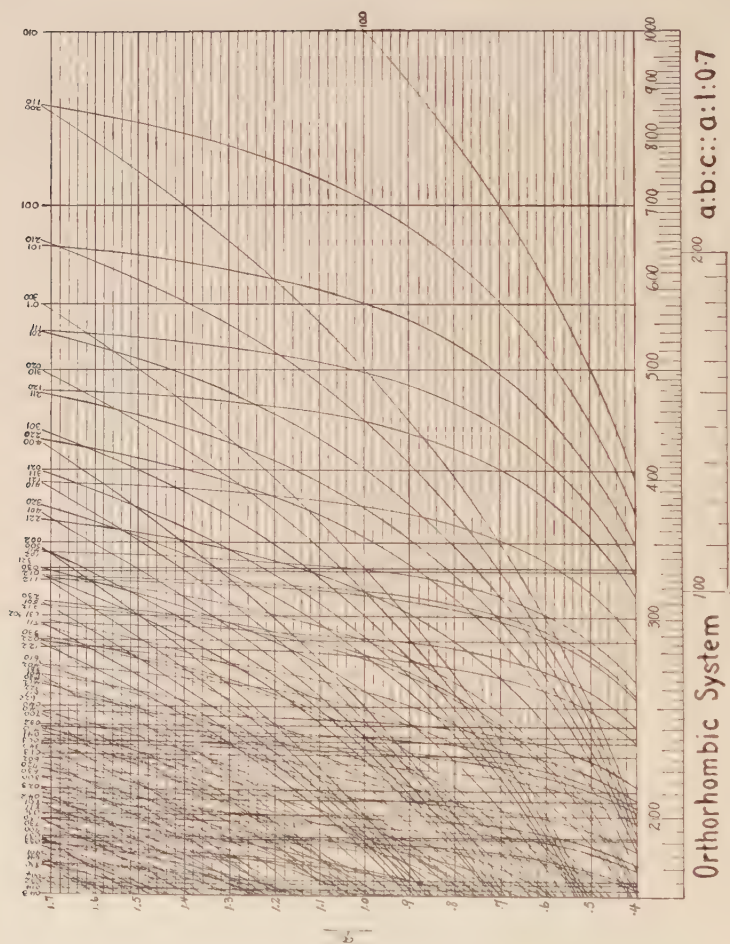


FIG. 28a.

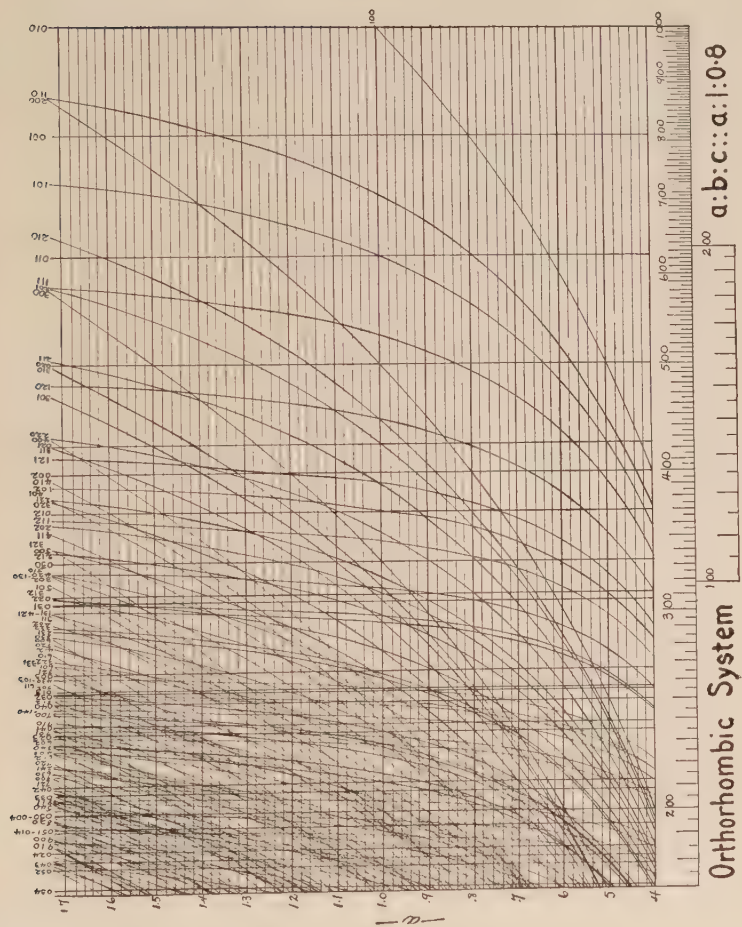
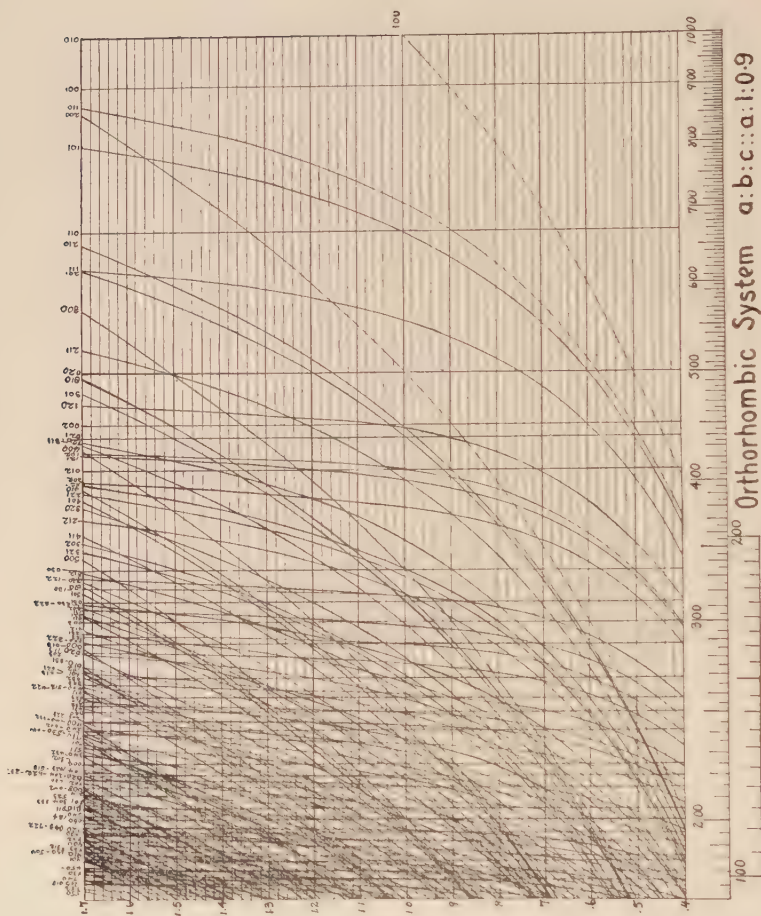


Fig. 28b.



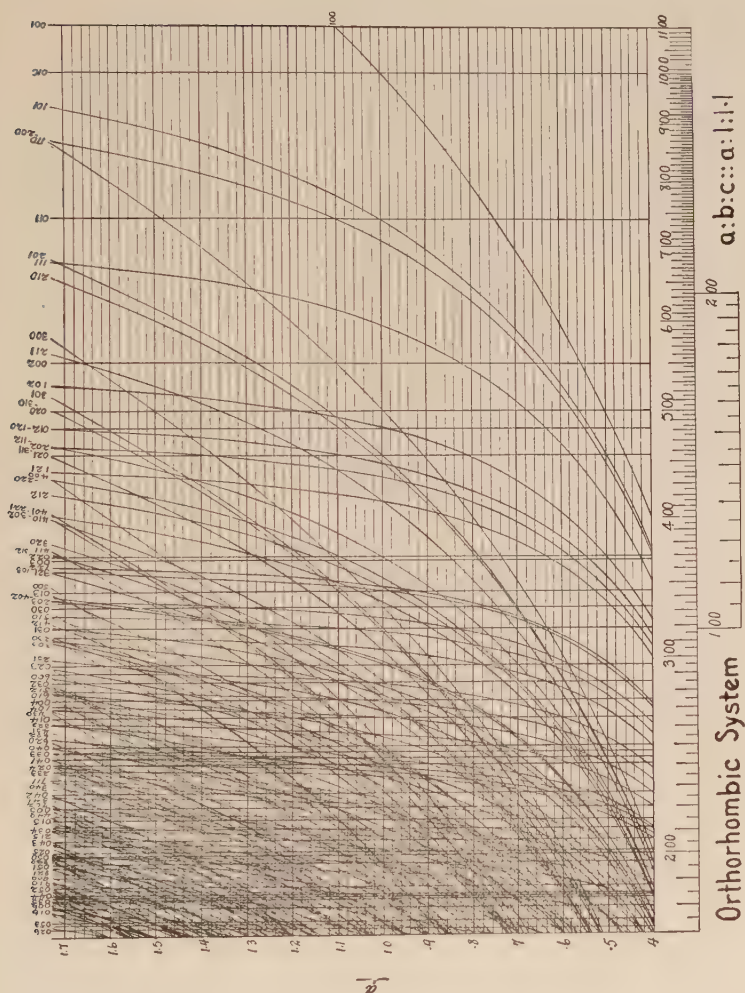


FIG. 28d.

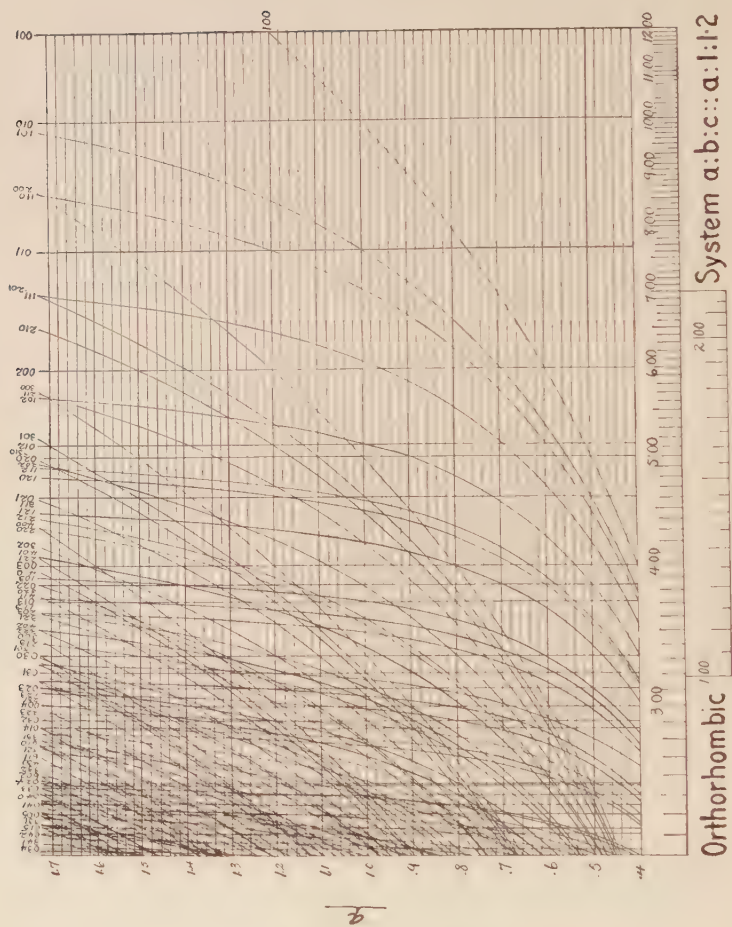


Fig. 28e.

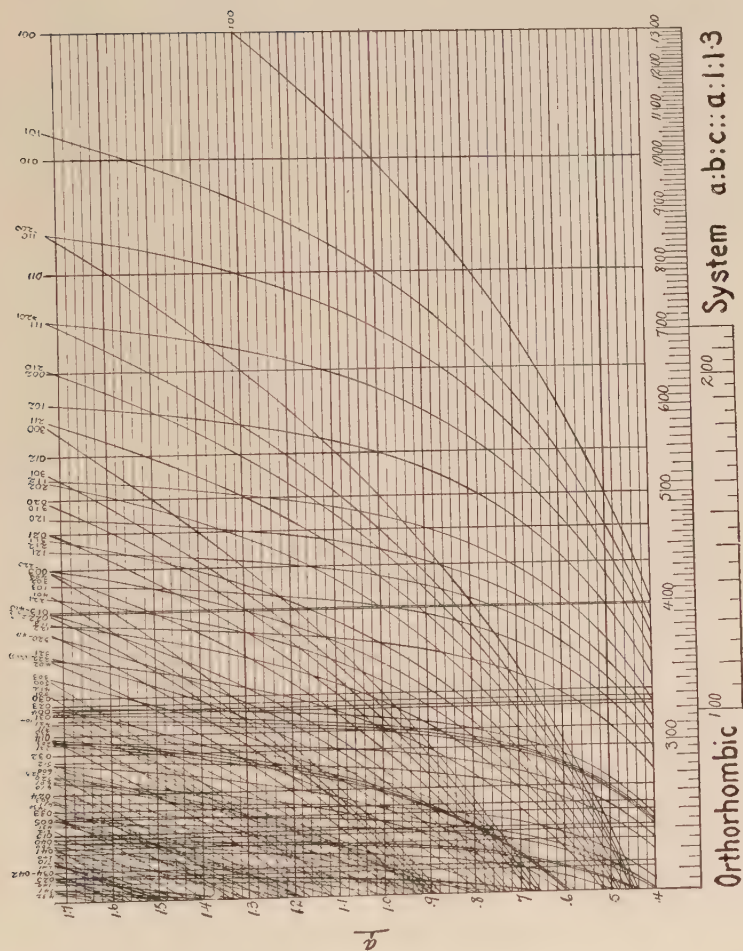
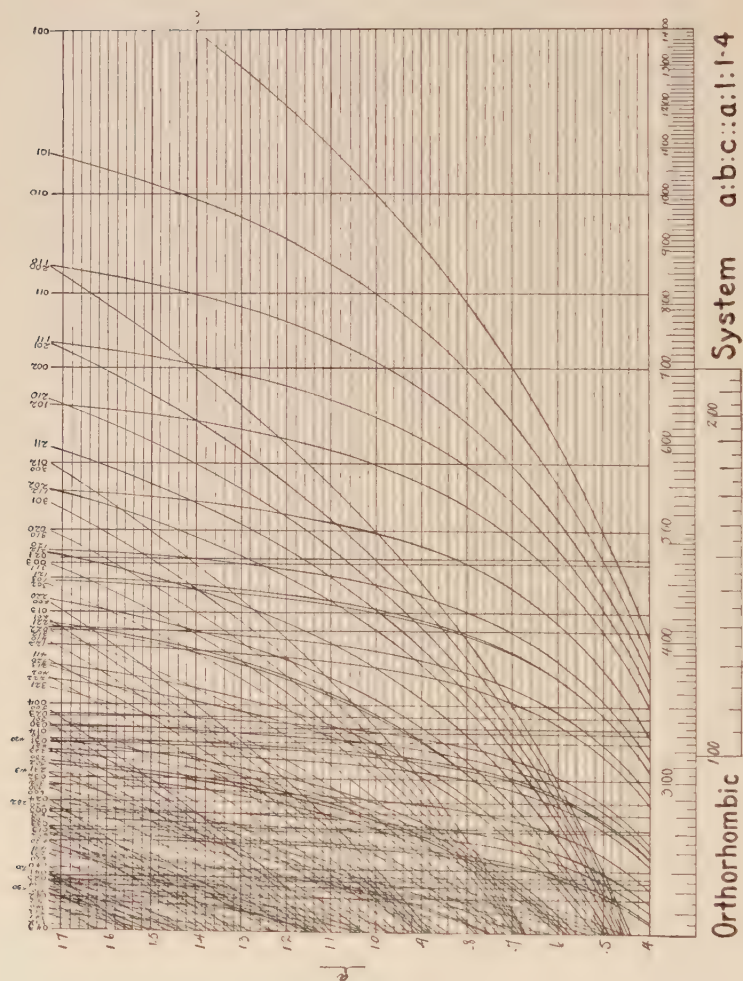
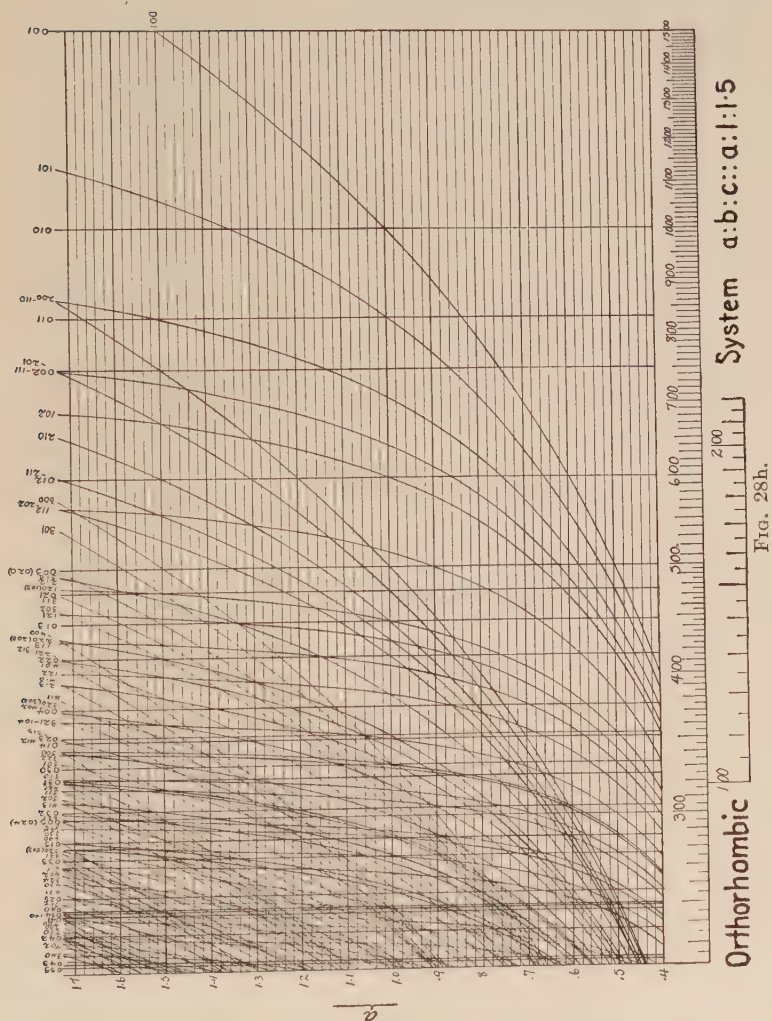


Fig. 28f.





0.7Å. In the case of some crystal structures, such as the face-centered cubic, an angle corresponding to 0.8Å. is sufficient. The number of lines in a diffraction pattern of a powder is greater the shorter wave length of X-rays employed, for the smallest interplanar distance which will diffract the rays is, from Eq. (1),

$$d = \frac{1}{2}\lambda$$

The longer wave lengths, such as are characteristic of iron and copper, give more accurate determinations of the larger interplanar spacings and, in special cases, have considerable real advantage for such purposes. The wave length for Fe is too long to give enough lines for the satisfactory solution of crystal structures even when the X-rays are bent through an angle $2\theta = 180$ degrees. The wave length for Cu requires 180 degrees for an interplanar distance of 0.77Å. Both wave lengths are so long as to require a special window on the X-ray bulb, and this, in turn, necessitates operating the tube while it is connected to the pump. The objections to this are obvious to anyone who has ever tried it. The very short wave lengths, such as are characteristic of W, $\lambda = 0.2\text{\AA}$., give angles of diffraction which are so small as to interfere seriously with accuracy of measurement, especially on a photographic film. An interplanar distance of 0.7Å. bends these rays through an angle of 2θ of only about 16 degrees. The upper left-hand corner of Fig. 22c shows that, in extreme cases, at least, there is a practical limit to the number of lines in a diffraction pattern which are useful in solving a crystal structure by the ordinary graphical methods, so that we are led to the conclusion that the short wave lengths from W, Pt, etc., are ordinarily of little value in crystal analysis by the powder method. The wave lengths which are characteristic of molybdenum, rhodium, or silver are sufficiently penetrating to permit the use of an all-glass X-ray bulb which has been pumped out once for all and sealed off from the pump. An interplanar distance of 0.7Å. corresponds to an angle 2θ of about 60 degrees for Mo rays. This means that if a photographic film is bent on an arc of 8-inch radius, interplanar distances of 2.0Å. can be determined to 0.25 per cent, and distances of 1.6Å. or less can be determined easily to 0.1 per cent. Greater accuracy is rarely useful, because the traces of impurities ordinarily found in even "chemically pure" materials seem to make variations from sample to sample of

the order of 0.1 per cent in the parameters of crystals from different sources. For instance, the side of the unit cube of 99.9 per cent Ag is $4.058 \pm 0.004\text{\AA}$., while the value for 99.999 per cent Ag is $4.079 \pm 0.004\text{\AA}$.¹ Considerations of this sort, coupled with the fact that the X-ray tube itself imposes certain limitations upon the choice of a target material and, therefore, indirectly upon the choice of a filtering material, have led users of the powder method in this country to the almost exclusive use of Mo alpha rays, a radius of curvature of the photographic film of 8 inches, and an exposure time sufficient to show a diffraction pattern throughout an arc of at least 60 degrees.

¹ DAVEY, W. P., *Trans. Am. Soc. Steel Treating*, Vol. VI, p. 375, 1924; *Phys. Rev.*, Vol. XXV, p. 375, 1925.

CHAPTER IV

PRACTICAL PHOTOMICROGRAPHY

BY R. P. LOVELAND AND A. P. H. TRIVELLI

The chief limitation on photomicrography as compared with visual microscopy is that the photomicrogram is restricted to that area which is simultaneously in focus in the plane of the ground glass, *i.e.*, by the flatness of the field of the optical system. Now, it is a law of physics that the resolving power of an objective, which is the power of forming distinctly separated images of the lines or dots composing detail, is *inversely* proportional to its depth of focus. So, while depth of focus, hence, flatness of field, can be gained by restricting the working aperture of the objective, as by closing a diaphragm in the illuminating beam, yet resolution is always lost. Fortunately, flatness of field depends upon the whole optical system; and resolution, on the objective alone. By use, therefore, of a negative lens, useful only for photomicrography—the Zeiss *Homal* and the Bausch and Lomb *Ampliplane*—it has become possible to form a flat image of a very much greater area than ever before.

Mounting the Sections.—A convenient and simple mount for pieces of ore with only one polished surface consists of a brass cylinder, about 2 inches in diameter and 1 inch deep, to which a bottom has been brazed. On this bottom, a lump of modeling clay is placed, the specimen stuck on top and carefully pressed down by a piece of plate glass until the latter rests on the rim of the cylinder. The surface of the specimen is then parallel with the base of the mount and, when placed on the stage, is perpendicular to the axis of the microscope.

If the stage is not focusing, it is convenient to mount the specimen in plasticine, which is held in a hollowed rubber stopper. If this is inserted in the ring which ordinarily holds the substage condenser, the polished surface can be alined correctly by pressing it against the back of a microscope slide which is clipped to the stage. The condenser rack can be used for the coarse focusing adjustment.

Methods of Illumination.—In mineralogy, the specimens may be either transparent, thin sections or opaque masses. For the former, the microscopical set-up and procedure are similar to those generally used by biologists, etc., and have been thoroughly and competently described in a number of books. Methods of opaque illumination have been less comprehensively treated, although most of the general principles may be applied to either. The methods of opaque illumination may be classified as:

1. Oblique
2. Vertical or specular
3. Conical
4. Combinations of above

Oblique illumination presents the material by the method usually employed in vision. On the other hand, in microscopy, it presents an insidious danger. Oblique illumination, from one side, produces shadows that with higher powers not only conceal detail but are also sometimes so deceptive that they cannot be distinguished from true detail. Moreover, the maximum resolution cannot be obtained by oblique illumination.

The result of vertical illumination, which is axial and, therefore, specular, is the antithesis of that obtained by oblique illumination. The highlights of the former are the dark patches of the other, since vertical illumination exhibits the angles of the planes of the surface of the specimen. It requires experienced judgment to interpret correctly the results of such illumination. For highly polished reflecting surfaces, as in metallic ores, it often is far superior, however. Moreover, the highest resolving power of the objective may be utilized.

If the focused illumination is intercepted by a central stop forming a hollow cone of light, so-called *conical illumination* is obtained, with which have been realized some remarkable results showing almost stereoscopic relief. Usually, the shadow is made eccentrically, giving a combination with oblique illumination.

Low Magnification.—With low magnification, the problem of illumination becomes simply one of obtaining a sufficiently large field evenly illuminated. Oblique lighting is the more usual for very low magnifications and, with the long working distance, is usually obtained by focusing the light directly on the specimen by means of a bull's-eye condenser. The angle and direction of the light is a very influential variable, the best position being determined by trial. For 16- and 8-millimeter objectives, a

silver reflector attached to the objective may be used to reflect the low-angled cone of light upon the object. In order to obtain more even lighting without sharp shadows, it is well to put the specimen in a white box with one side cut away to admit the light; or a piece of white paper may be curved around the specimen to reflect side lighting. Even two illuminants may be used. With 32- to 8-millimeter objectives, the Beck applanatic

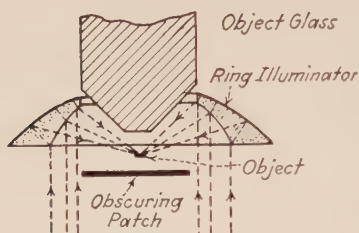


FIG. 1.

ring illuminator is most satisfactory. The specimen, which must be small, is mounted on a glass slide, and the microscope set as for transparent photomicrography (Fig. 1). Special objectives should be used so as not to obstruct the reflected light. For larger objects, the Silverman illuminator may be

used. This is an attachment providing an illuminated wire concentric with the front of the objective. Rather long exposures must be given, and the illumination is not at all critical.

It is also possible to lead the light directly to the field through a quartz or glass rod utilizing the phenomenon of internal reflection. If one end of such a rod is illuminated, the light will pour out of the other end as long as the critical angle is not exceeded by a too-sharp bend.

Low-power vertical illumination is best accomplished by interposing a piece of cover-glass in front of the objective and at an angle of 45 degrees to the optic axis. The light beam which is at right angles to the microscope axis should be focused so that, after partial reflection at the glass surface and then by the object, it is in focus on the objective.

For low magnification, the microscope objective can be advantageously displaced by a micro-Tessar, which is a photographic lens requiring no ocular. In this case, it is best to remove the inner tube of the microscope, since the field is limited by its circumference. The advantage of the specially large microscope tube is most evident in this case. In fact, the microscope may even be dispensed with and the micro-Tessars fitted directly to the camera. It will probably be necessary to line the tube with coffin paper or other black material to cut out the flare caused by reflections. Special adapters for the camera for very low-

magnification photography are made by most microscope manufacturers.

Medium and High Powers.—When the working distance of the objective becomes small, it is no longer possible to illuminate the object directly or to interpose a cover-glass. Instead, the objective itself must be used as a condenser. This is done with the so-called *vertical illuminators* in two general ways. Either a thin bit of plane glass is placed at an angle of 45 degrees behind the back lens of the objective, or a mirror or prism is used which allows the image-forming light to pass up through the unobstructed portion. The problem with such an illumination system is to obtain even illumination over the required field and to reduce the effect of internal reflections. This last is very serious, particularly that caused by partial reflection from the surface of the back lens. The reflector, therefore, should be as near this lens as possible. The special objectives made thus for use with vertical illuminators should be used. A bit of coffin paper glued to the straight edge of the mirror and bent so as to lie in the plane of the optic axis materially aided in reducing the internal reflections by preventing light from flaring out to the other side of the back lens where it is reflected back to the ground glass. The inside of the objective and illuminator should be a dead black, so that the reflections can be directed against the side and absorbed. The R. & J. Beck Company, of London, are marketing reflectors which are curved in order to aid in the diverting of the undesirable flare to the sides.

The mirror gives far brighter images than the plane glass, with much more contrast. On the other hand, it is very difficult to obtain even illumination, since a flare is formed over the half of the image behind the unobstructed portion of the objective. But the most fundamental drawback is the fact that it necessarily cuts down the aperture and therefore decreases the resolving power. Moreover, because of its shape, resolution is greater in one direction than the other, being greatest in the direction of the edge of the mirror. This means that fine laminas may be resolved if lying in one direction, whereas in the other, they would appear as a single mass. A mirror or prism reflector, therefore, should never be used for the highest powers unless great contrast is absolutely essential. While the plane glass reflector allows use of nearly the full aperture, unfortunately there is produced over the whole image a uniform flare which is

so great that it may hide detail if the object contains little contrast.

Critical illumination, i.e., forming an image of the light source in the plane of the object, is, theoretically, the best form of illumination, as it, also, is with transparent specimens. It may be obtained by placing the illuminant at the same distance from the reflector as the latter is from the ocular. Practically, however, it is best to interpose a bull's-eye condenser and focus it on the object so that it will be acting as a large, evenly illuminated light source, and this is also the practice with transparent specimens. If the tube of the vertical illuminator is provided with a lens, as is often the case, it is necessary to set up an optical system whereby an image of the bull's eye is thrown by this lens onto the field through the objective. An iris diaphragm should also be provided, to cut out all light not actually used in the image.

The special objectives for such illuminations are designed for use without cover-glass if dry. Correction should be made in the tube length for the increase caused by the insertion of the illuminator.

H. S. George¹ developed a method for obtaining results with a vertical illuminator and plane glass reflector similar to those obtained by oblique illumination with low powers. He secured conical illumination by interposing in the center of his cone of illumination a cardboard disc, which gave a marked disc eccentrically. Since this oblique illumination casts shadows, it is necessary to know from which direction the light comes when interpreting the picture. L. E. Jewell,² utilizing this idea, has developed an illuminator that uses a stellite mirror which slides lengthwise and contains an elliptical hole at one place in the edge. Thus, anything from a half-hollow cone of light to full specular illumination can be obtained. An iris diaphragm below the reflector aids in controlling the illumination.

For small specimens, the Beck aplanatic ring illuminator³ has been adapted for higher powers. It has even been adapted to

¹ GEORGE, H. S., "Conical Illumination in Metallography," *Trans. Am. Soc. Steel Treating*, Vol. IV, No. 2, pp. 140-161, August, 1923.

² JEWELL, LEWIS E., "An Illuminator for Use in Metallographic Microscopy," *Jour. Optical Soc. Am.*, Vol. XIV, No. 2, pp. 159-167, February, 1927.

³ BECK, CONRAD, "Modern Methods of Microscope Illumination," "High-power Opaque Illumination," *Jour. Sci. Instruments*, Vol. I, May, 1924.

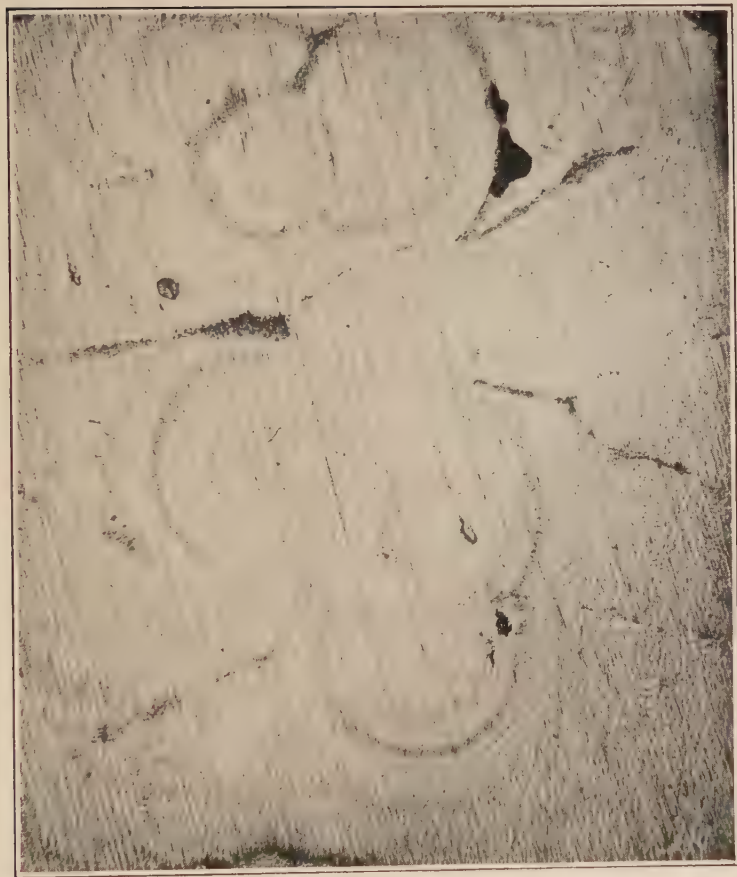


PLATE I.—Malachite magnification $25\times$ green filter relief illumination, note scratches. (*Photograph by L. E. Jewell.*) Compare with Plate II.



PLATE II.—Malachite same field as Plate I. Magnification 25 \times . Green filter. Diffused oblique illumination (Jewell's method). Note that scratches no longer show. (*Photograph by L. E. Jewell.*)

immersion objectives by making their front mounting of glass.

Oblique illumination is not adapted to flat, highly polished surfaces. These are better displayed by specular or vertical method.

THE USE OF COLOR FILTERS IN PHOTOMICROGRAPHY

The spectrum of the illumination in photomicrography is almost invariably controlled by the use of color filters. Such filters are used for (1) the control of contrast of the image; (2) the improvement of definition; (3) the increase of resolution; (4) the correct rendition of color.

1. The Control of Contrast of the Image.—Whereas the *white* light of the illuminator is a combination of the whole spectrum

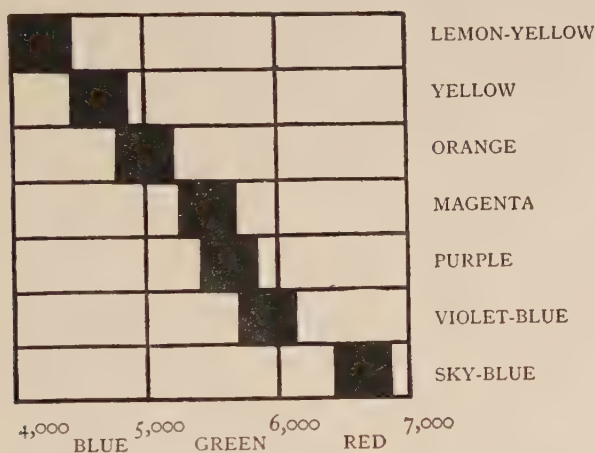


FIG. 2.—Residuals and position of absorption bands.

from the ultra-violet to the infra-red, the light transmitted or reflected from a colored object has had a portion removed by absorption. The color of the object, therefore, is complementary to that absorbed. Let us imagine a single absorption band, about 400\AA . wide, to pass over the spectrum from the red end and observe the color of the residual combined light. When it absorbs in the pure red only, from 6,500 to 6,900, the color of the residuum will be a sky blue. If it removes the orange, absorbing from 5,800 to 6,200, the color will be light, violet blue. As it shifts down the spectrum into the yellow green (5,600 to 6,000), absorbing no red, then down into the green (5,200 to 5,600), the

color changes into a bluish purple, then becomes reddish until it is magenta. As the band shifts toward the blue, the magenta becomes a sort of orange, at 4,700 to 5,200, then becomes more yellow, until, finally, it is lemon yellow (see Fig. 2). It may be seen that it requires two absorption bands removing both ends of the spectrum to give a green color. While natural objects very rarely have sharp absorption bands, these same principles apply.

It is clear that if we illuminate an object solely by that range of light which it completely absorbs, it will appear absolutely black against its illuminated background and we shall have gained the greatest possible contrast. Our first rule is, therefore: To obtain maximum contrast of a colored object against its background, illuminate it with its complementary color. Its background may consist of the rest of a specimen. Such great contrast, however, is rarely desired, since all detail will tend to be blocked out in the general blackness. A filter with an overlapping absorption, then, is much preferable. The simplest procedure for the inexperienced is first to interpose the filter giving maximum contrast and then successively substitute others which pass more and more light outside the absorption bands of the specimen until the desired contrast is obtained, as determined by visual inspection of the ground glass. Do not overdo contrast.

On the other hand, if the specimen is of one color, but full of detail, the problem is to gain contrast within the object and to reduce it against the background. This gives us our second rule: To reduce contrast and gain detail *within* a colored object, illuminate it with light of the same color.

The color filters may consist of colored glass, liquid solutions, or dyed films, usually gelatine. It is dangerous to depend upon the visual color of a medium as a criterion, since it is the absorption spectrum which is essential and this may vary widely with little visual change. Blues or greens, for instance, may or may not have transmission bands in the red. Although glass is the most permanent and convenient, there are few good glass filters. Certainly, the range of glasses with appropriately controlled absorption spectra is insufficient. Liquid filters, however, are practical, and they are widely used although considerably more inconvenient. Saturated solutions of metallic salts can be used, their absorption being determined with a hand spectroscope. Dye solutions give satisfactory results in concentrations of

1:1,000. A saturated solution of picric acid effectively cuts out all blue but gives high transmission above $5,000\text{\AA}$. The Gifford F line filter is a popular one with a green transmission band. It consists of a solution of malachite green in pure glycerine and a piece of peacock-green glass to cut out a red transmission band. This filter, however, will greatly prolong exposure. Directions for making a variety of liquid filters is given both in Barnard and Welch and in Hind and Randles.¹

The widely used gelatine filters, however, offer a convenient set of accurately known and published transmission bands covering the entire spectrum. They are usually cemented between two pieces of optical glass and, in most cases, are so stable to light as to last indefinitely if given reasonable care. They should be kept clean, but under no circumstance should water be allowed to come in contact with them. Breathing on them and rubbing with a soft cloth is usually sufficient. It should be remembered that xylol and alcohol are solvents for the balsam cement. If wet with any of these, air may get in and ruin the filter. The Eastman Kodak Company publishes a booklet² giving the absorption spectra of about one hundred Wratten color filters, including, in many cases, the prolongation of exposure required. Nine of these, the so-called *M* filters, have been selected as of especial value to microscopists. This set includes

Name of filter	Visual color	Spectral transmission
A.....	Orange red	From 5,800 to red end
B.....	Green	From 4,600 to 6,000
C.....	Blue violet	From 4,000 to 5,100
D.....	Purple	From 3,800 to 4,600 and from 6,400 to red end
E.....	Orange	From 5,600 to red end
F.....	Pure red	From 6,100 to red end
G.....	Strong yellow	From 5,100 to red end
H.....	Blue	From 4,200 to 5,400
K.....	Pale yellow	

¹ BARNARD, J. E., and F. V. WELCH, "Practical Photomicrography," Longmans, Green & Company, New York, 1925.

HIND, H. L., and W. B. RANGLES, "Handbook of Photomicrography," E. P. Dutton & Company, New York, 1913.

² *Photomicrography*, Eastman Kodak Company, Rochester, New York, 1925.

By using these filters in pairs, the spectrum can be divided into 10 portions that may be used to approximate monochromatic light.

Filters	Dominant wave length	Visual color
D and H.....	4,500	Violet
C and H.....	4,800	Blue
B and C.....	5,050	Blue green
B and H.....	5,200	Bluish green
G and H.....	5,350	Pure green
B and G.....	5,500	Yellowish green
B and E.....	5,750	Greenish yellow
A.....	6,000	Orange red
F.....	6,250	Pure red
A and D.....	6,600	Deep red

The following filter factors for Wratten panchromatic and Eastman orthochromatic plates for artificial light will give an idea of the relative values. For other plates or films, the factors can be determined by trial exposure.

M FILTER FACTORS

Filters	With panchromatic films or plates		With orthochromatic films or plates	
	Tungsten	Carbon arc	Tungsten	Carbon arc
25 A.....	6	10		
58 B.....	12	13	14	20
49 C.....	16	13	10	9
35 D.....	Used only in combination			
22 E.....	5	8	20	30
29 F.....	10	18		
15 G.....	3	4	12	20
45 H.....	10	7	10	8
6 K1.....	1½	1½	2½	3
D + H.....	80	50	35	30
C + H.....				
B + H.....	150	120	250	200
G + H.....	1,800	1,800	1,800	1,800

2. The Improvement of Definition. The images formed by the various colored rays through a simple lens are focused in

separate planes, one behind the other. Approach to monochromatic light will, therefore, obviously improve the definition of the photographed image. Achromatic objectives are usually corrected for this defect at two wave lengths and for spherical aberration, at one wave length which usually lies in the yellow green, the brightest color to the eye. If other conditions allow, therefore, it is best to use such a filter as the green Wratten *B* to gain the sharpest image. Although apochromatic objectives are chromatically corrected for three colors and spherically for two, making good images with white light, their field is much less flat. They are, also, much more expensive. Almost equally satisfactory results may be obtained, fortunately, with the achromatic objectives when used with color filters. In fact, achromats should never be used photographically without filters.

3. The Increase of Resolution.—For high-power work, the limiting factor is resolution, not magnification. The ocular merely magnifies and separates the details already resolved by the objective. When the lens of the objective is filled with light, the distance between two lines just resolved, *i.e.*, optically separated, is

$$D = \frac{\lambda}{2 \text{ N.A.}}$$

where λ = wave length of the light employed,

N.A. = numerical aperture of the objective.

The shorter the wave length, therefore, the better the resolution. Since the numerical aperture of the objective is a fixed constant (1.4 N.A. is about the limit of modern immersion objectives), we must rely on shortening the wave length to increase resolution.

Thus, with an N.A. of 1.0 and a red Wratten *F* filter, we should be able to see 80,000 lines to an inch; with a green *B* filter, about 95,000 lines to an inch; while with a blue *C* filter, 100,000.

The *H* filter is very useful for increasing the resolving power, since it is somewhat easier to focus than the blue *C*.

4. The Correct Rendition of Color.—Correct reproduction of color is rarely desired by the microscopist. It is usually much more important to obtain the best contrast to show the details, and the two may be antagonistic. It is sometimes wanted to portray colored minerals, however. A light-yellow filter specially adjusted to the panchromatic photographic plate must be used. If an arc light is used, a yellow filter, such as the Wratten *K*₂, is

needed for that purpose. It is evident that an apochromatic objective should be used if possible.

PHOTOGRAPHIC PROCEDURE

Materials.—It has been assumed, in the above discussion, that films or plates are used which are sensitive to the colors transmitted by whatever filters may be selected. Photographic plates and films are divided into three classes, with regard to color sensitivity: (1) ordinary materials with only the ultra-violet-to-blue sensitiveness of the silver halide, (2) orthochromatic materials whose sensitivity has been extended into green by a sensitizing dye; and (3) panchromatic films or plates which have been made sensitive to the whole visual spectrum. This last class is most useful to the microscopist, since it allows him complete control over the contrast of his specimen with a wide selection of filters. Without the added sensitiveness in the green and red afforded by such plates, most of the commercial filters for photomicrography either become useless or the exposure factors are very greatly increased. In the Wratten *M* set, the *B*, *C*, *G* and *H* filters are still useful with orthochromatic materials.

It must be remembered that visual judgment of contrast of the ground-glass image will not correspond to the photographic result unless panchromatic material is used.

Photographic plates and films vary widely in their characteristics, being made to serve many widely different purposes. That this is not always fully realized is evidenced by the mischoice that is sometimes made in selection of the type required for this purpose. Plate speed is not of great importance in photomicrography. The important factor is contrast. Usually, the mineralogical microscopist desires a fine-grained process emulsion which will grant considerable contrast in the negative. The most suitable plate for general work in microscopy is one that will yield good negatives with a widely varying degree of contrast with different development times, giving very high contrast if desired. It should also be panchromatic, although orthochromatic plates are sometimes sufficient.

Exposure.—The many factors involved in determining the exposure time make the correct calculation of its length a complicated process. Fortunately, with each worker, some factors usually remain constant, although the nature of the object itself is one of the most puzzling variables. Probably the best,

and certainly the simplest, procedure is to make a trial exposure for each type of specimen as it is encountered, under definite conditions, using no filters or the one to be used if that is definitely known. Then the magnification, filter, or the N.A. of the objective can be varied, and the resulting exposure calculated: $\text{Exposure} = \text{Standard exposure} \times \text{Factor for magnification} \times \text{Filter factor} \times \text{Factor for N.A.}$

The exposure varies directly as the square of the magnification.

The exposure varies directly with the filter factor.

The exposure varies inversely as the square of the N.A. If the field is illuminated through the objective, as in vertical illumination, this last relation fails. Since the objective is also acting as a condenser, the exposure varies little with change of objective at the same magnification.

The trial exposures may be made on a narrow strip of plate, the rest being reserved for similar trials. The plate should be exposed in a series of steps varying in time in geometrical progression. For instance, expose the whole strip for 1 second, push in the slide for a short distance and expose for another second, push it in another step and expose for 2, 4, 8 . . . seconds successively until the slide is completely in. If the whole plate is badly underexposed, repeat, using minutes for units.

Development.—While the customary red safe lights may be used with orthochromatic materials, they are obviously useless for panchromatic plates, for which special precautions must be observed. Although it is, of course, safest to handle them in total darkness, the manufacturers of such plates provide a special green safe light, which, although, seemingly too faint for help at first, is adequate when the eye is accommodated to it. It must be kept in mind that a safe light is merely controlled colored illumination whose fogging action on specified photographic materials is negligible at a definite distance for a reasonable length of time. Plates should not be held up immediately before them for inspection.

While there are several general methods of photographic development, that most suited to photomicrography is development to a specified time at a definite temperature according to the degree of contrast desired in the negative. In fact, that is the only method which can be used with panchromatic plates, since they would fog if illuminated enough for inspection. For timing development, either a clock with large hands or, more

conveniently, a special time meter which will sound a signal at the expiration of the time can be used.

Development may be by either tray or tank. For routine work where many negatives will be handled, the latter is far preferable. To develop a plate in a tray by time, proceed thus: Get the dishes, developer, clock, etc., ready, and have a cover ready for the developing tray; pour some developer into the tray to a depth of about $\frac{1}{2}$ inch, turn on the safe-light lamp, and turn out the white light; immerse the plate quickly and evenly, which can be done by tipping up the tray on its long edge, dropping in the plate, and causing the developer to flow back in one quick wave by lowering the tray; cover the tray immediately and observe the time or start the time clock; rock the tray gently for the time specified by the manufacturer of the plate to gain the desired degree of contrast; then quickly remove the plate or pour off the developer and rinse and fix the plate.

For tank development, a suitable developer is kept in covered tanks sold for the purpose, and the plates or films are dropped or clipped into special development hangers. These are then dropped into the tank and kept in motion throughout development, then removed and used also during fixing and washing. Anywhere from one to a dozen plates can be satisfactorily and simultaneously developed thus, if the movement during development is such as to separate the plates individually. It is possible and, after practice, quite simple to work in complete darkness.

Each maker usually publishes with each box of plates the best developer for use with them. In the case of panchromatic plates, the maker should enclose with each box information regarding the correct development time for those particular plates, since it varies somewhat from batch to batch of emulsion. The following developer has proved to be eminently satisfactory for either tray or tank development and keeps remarkably well:

PROCESS DEVELOPER

	Avoirdupois	Metric
Hot water (about 125° F.).....	16 ounces	500 cubic centimeters
Metol or elon.....	15 grains	1 gram
Sodium sulphite.....	2½ ounces	75 grams
Hydroquinone.....	135 grains	9 grams
Sodium carbonate.....	¾ ounces	25 grams
Potassium bromide.....	75 grains	5 grams
Cold water to make.....	32 grains	1 liter

For great contrast, use full strength; for less contrast (commercial plates), dilute with an equal volume of water.

Fixing and Washing.—With the following acid fixing bath, the light can be turned up after fixing for 3 minutes (plates should be fixed twice the time for the milkiness to disappear):

	Avoirdupois	Metric
Hypo.....	16 ounces	250 grams
Water.....	64 ounces	1 liter

When completely dissolved, add the following hardening solution:

	Avoirdupois	Metric
Water.....	5 ounces	75 cubic centimeters
Sodium sulphite.....	1 ounce	15 grams
¹ Acetic acid (28 per cent pure).....	3 ounces	45 grams
Potassium alum, powdered.....	1 ounce	15 grams

¹ Glacial acetic acid may be converted to 28 per cent acid by taking 3 ounces of glacial acid and adding 8 ounces of water.

To make up the hardener, dissolve the chemicals in water at about 100°F. in the order given above. The sodium sulphite should be completely dissolved before adding the acetic acid. Pour the hardener solution slowly into the cold hypo solution while stirring the latter rapidly.

Agitate the films or plates on first placing them in the bath and at intervals thereafter. The bath should be discarded when a white sludge appears, or the rate of fixation becomes notably longer. The plates should always be rinsed between development and fixation. This not only prolongs the life of the bath but also avoids stains and other troubles. The rinse bath of water should lie between the developer tray or tank and the fixing tank.

After fixation, if the plate is given a separate preliminary rinse, it will be completely washed after 10 minutes of clean, rapidly running water or five changes of water for 2 minutes each.

Printing.—Glossy paper is generally preferred for printing, since it shows the detail best. It should always be used if the print is for publication and is improved for the purpose by drying on a ferrotype plate. Usually, a soft-contrast paper will be most useful.

Intensification or Reduction.—Since the microscopist has complete control over exposure and development, he rarely has need for either. It is sometimes desirable to obtain a brighter

negative by slight application of Farmer's Reducer, which tends to add contrast and remove any slight veil of fog. It is made by adding a few drops of strong potassium ferricyanide solution to a 30 per cent solution of plain hypo. When it is reduced sufficiently, wash the negative thoroughly.

Color Photomicrography.—Mineralogical photomicrography particularly lends itself to color photography for the accurate reproduction of characteristically colored minerals or of polarization colors. The modern screen plate, such as the Autochrome or Duplex, furnishes a means so very much more simple than any other process and yet so adequate for transparencies and lantern slides that it alone need be considered except for very special purposes. Complete directions are furnished by the maker of the plates. Apochromatic objectives must be used together with compensating oculars or, even better, with the Zeiss Homal or Bausch and Lomb Ampliplane.

CHAPTER V

DIELECTRIC METHODS

BY ERNEST E. FAIRBANKS

Introduction.—Faraday was the first to investigate the properties of those materials for which he coined the name *dielectrics*. The name refers to the fact that two charges of opposite sign, positive and negative, can exist simultaneously on an insulator without mixing. Substances are commonly divided into conductors and non-conductors or dielectrics. The distinction between a dielectric and a conductor consists of the fact that in the space between two conductors, separated by a dielectric, a state of electric stress can exist without the continuous supply of energy which is required to maintain the condition of electric stress. No sharp distinction exists between conductors and dielectrics; in fact, it is probable that all dielectrics allow a very minute current to pass through them, although this may be beyond the sensitiveness of our measuring apparatus.

Many materials which are efficient dielectrics at ordinary temperatures gradually alter as the temperature is raised and change imperceptibly to a conducting state. In fact, at a temperature of about 2000°C. or less, insulating materials may be said to be almost non-existent. When conductivity commences in such materials, which include many minerals, it increases at a relatively very great rate with increase of temperature. It may increase twofold for every few degrees of temperature increase.

In the present application of dielectric methods, we are especially concerned with the determination of what is known as the *dielectric constant*. This value will be referred to as K in the following pages. We are, also, concerned solely with substances possessing for K a value which is easily determined. Such substances are referred to here as *dielectrics*.

K of a dielectric is the ratio of the capacity of a condenser made up of that dielectric: the capacity of the same condenser having air as the dielectric. K is taken as unity for a vacuum, but K for air is also nearly unity at atmospheric pressure and is,

therefore, taken as unity for nearly all practical purposes. K for air at 76-centimeters mercury pressure and at an infinite wave length is 1.000586.

The change of K with the change in the frequency of the current is important. Little change in K for many solids and liquids is produced over a range from 100~ per second up to very high values. Quartz, for example, shows a variation of not more than 1 or 2 per cent throughout the range in frequencies from 250 up to 3×10^7 ~ per second (wave lengths of 1.2×10^6 down to 10 meters). At very low frequencies, most substances show considerable decrease in K . Water which has $K = 81$, as ordinarily measured with infinite wave length, is reduced to 2 if measured with a wave length of 12 meters.

Since K is not the reciprocal of conductance, its determination presents, for mineral identification, additional and unique diagnostic data which, when used in conjunction with other data, have been found most useful. Table I is introduced to present a comparison between the range of electrical conductance and K for the same substances. It is possible to vary temperature in the measurement of conductance without producing any appreciable disturbance.

TABLE I.—SPECIFIC CONDUCTANCE AND DIELECTRIC CONSTANT
(Compiled from various sources)

Substance	Specific conductance	Temperature, °C.	Dielectric constant at 18°C.
Silver.....	6.0×10^5		
Hydrocyanic acid.....	1.1×10^{-7}	0	96
Water.....	4.2×10^{-8}	18	81
Methyl alcohol.....	8.0×10^{-7}	0 to 20	33
Ethyl alcohol.....	1.2×10^{-9}	17	26.1
Ammonia.....	3.8×10^{-10}	15	22
Sulphur dioxide.....	1.8×10^{-11}	..	16.5
Acetic acid.....	2.4×10^{-8}	..	9.7
Propionic acid.....	0.1×10^{-9}	..	5.5
Ether.....	7.1×10^{-16}	..	4
Benzene.....	$10^{-14} - 10^{-15}$..	2.3

Application of Dielectric Methods. In the application of dielectric methods to determinative mineralogy, it has been the writer's desire to extend determinative methods to the minute

materials which lie beyond the range of petrographic methods. Under the most favorable conditions, a crystal can be isolated and used for conoscopic observation when only 0.0065 millimeter in size. It is necessary, however, to have a strongly birefracting grain at this thickness in order to obtain a good interference figure. In the case of a weakly birefracting substance, a grain thicker than 0.01 millimeter is necessary in order to produce a path difference adequate to cause a visible contrast in intensity of field illumination sufficient to enable the observer to detect the changes in shape of the zero isogyres on rotation of the stage or of the nicols. Not only are dielectric methods applicable to many of the cases in which conoscopic observation fails to yield diagnostic data but they are also of value in the study of unusually fine material, which either gives aggregate polarization effects or is even too fine to yield refractive index data by a statistical method.

In the case of microchemical analysis, which is especially important in the determination of opaque minerals, the best means of identification of the microcrystals is by the application of petrographic methods. The grain size is, therefore, equally important in this method and with transparent mineral grains. Since the tendency in mineralogy is toward a thorough determination of mineral character and not merely a determination of a name, great care is necessary in the interpretation of micro-reactions. Isomorphous microcrystals would, in many cases, remain unrecognized, and the true character of the mineral from which they were derived would be incompletely understood, unless petrographic methods were applied to the study of such crystals. Unfortunately, opaque minerals commonly contain several elements which interfere in the microchemical reactions, making it either difficult or impossible to obtain microcrystals of sufficient size for optical study.

The reaction products which are formed as the result of the presence of interfering substances may lend themselves, however, to dielectric methods.

Since dielectric methods are strongly recommended here as aids in the determination of unusually fine mineral grains, it is advisable at least to mention the respective fields of X-ray analysis, dielectric methods, and petrographic methods. The limits of petrographic study have already been considered in this paper, but it is recognized that refractive index data can be

obtained from smaller grains than those required for conoscopic investigation. With regard to the application of X-rays, the following authoritative statement by Wyckoff¹ will be of interest:

Experience has shown that X-ray methods of analysis are rarely of value in case microscopic procedures can be applied. They, therefore, find their chief usefulness among preparations which are either opaque to ordinary light or are composed of crystals too small to be seen clearly under the microscope.

Wyckoff wrote the above with the limitations of petrographic methods clearly in mind but without any attention to the application of dielectric methods or to the possibility of converting opaque materials into transparent microcrystals by microchemical reactions. Obviously, the field is one of vast proportions between the crystule or unit cell treated by X-ray methods and the grain from which K can be first obtained. Dielectric methods are able to enter this field only slightly beyond the point where microscopic methods cease to be of value. This added range brings us to the limit of resolution. Since a vast amount of work remains to be done with reference to the material which can be easily resolved by the microscope, it undoubtedly will be some time before mineralogists ignore this field completely for the new one made available by X-ray methods. No attempt is being made to minimize X-ray analysis: The importance of such methods to the mineralogist cannot be overestimated.

One source of error remains to be considered before the details of the method recommended for the determination of K are presented. This is the presence of water, usually referred to as *absorbed water*, which produces large variations in K according to the amount present. In this connection, the following experiment with stilbite is instructive: K was determined for stilbite which had been subjected to conditions of very low humidity for several days, and the determination was made at 31°C. with an infinite wave length; the highest value obtained was 22; the mineral was then heated to 100°C. for 3 hours, and K was found to have increased from 22 to above 36; the optical properties were found to have remained unchanged, and it is probable that

¹ WYCKOFF, RALPH W. G., "Crystal Structure in Its Relation to Chemical Problems," lecture delivered at Columbia University, 1926. Published as Paper 624 of the Geophysical Laboratory, Washington, District of Columbia, pp. 11-12.

they do not change until the inversion to the orthorhombic form is reached, which occurs at about 250°C.

Method of Determining Dielectric Constant.—Single-phase alternating current with a range from 100 to 340 cycles arranged so that the voltage could be altered from 100 to about 400 was used by the author. The arrangement used in the determinations was adopted from Hatfield.¹

A fine nichrome wire is coiled around the bottom of a very small Florence flask and then brought to incandescence by means of house current. The bottom of the flask drops off and, due to its greater depth, is to be preferred over a watch glass. Two needles are set in a pen holder in such manner that a small gap exists between the points. The needles are connected to the current and insulated so that the holder can be easily handled. Two burettes mounted on a burette stand are to be recommended as the most convenient means of mixing liquids used in the tests. A binocular microscope is necessary for observation of the tests. It should be one of the new improved Greenough type which all manufacturers offer at the present time. Either Spencer, Leitz, or Zeiss is best suited on account of higher magnifications.

For the range of K between 2 and 36, kerosene and nitrobenzene, as recommended by Hatfield, are satisfactory. The K of any mixture of the two liquids is easily determined.²

When mixing liquids, great care must be taken to insure their thorough mixing. This can be accomplished simply by stirring with a glass rod.

Distilled water with $K = 81$ is a very useful liquid. Minerals possessing a K much greater than 81 will bridge the needle gap and form an arc. In case K is greater than 81 but not infinitely greater, the particles may bridge the gap but never produce an arc. Rutile will bridge the needle gap in water but does not produce an arc. K at $\lambda = 75$ is 110.

¹ HATFIELD, H. S., "Dielectric Separation: A New Method for the Treatment of Ores," *Bull. Inst. Mining Met.*, London, pp. 1-8, February, 1924.

² The following example may be of value: 2.3 cubic centimeters of nitrobenzene mixed with 1.00 cubic centimeter of kerosene proved to have the proper K for the highest value of a mineral being studied. K for this mixture is obtained by multiplying 2.3 by 36—the K of nitrobenzene—then adding 2—the K for kerosene—to the product. This gives 84.8. Dividing this figure by 3.3—total number of cubic centimeters involved—we obtain $K = 25.44$.

The method of determining the K —highest value—of a mineral follows: The mineral is ground to a very fine powder in a small agate mortar such as is used in microchemical work. The grinding is continued until further reduction appears imperceptible. Experience indicates that the grain size developed by this method of crushing is roughly constant between most minerals. If the material is opaque or nearly opaque in character, the liquid for the first trial may well be water with $K = 81$. If considered within the range 2 to 36, which catches most transparent minerals, the first trial can be made with nitrobenzene ($K = 36$). The highest value is taken as the point at which the mineral is attracted and beyond which it ceases to be attracted. Hatfield claims that he can separate particles differing in K by only 0.1.

If a separation for microchemical analysis is to be made, a smaller glass, such as a small watch glass, is placed in the liquid, and the material attracted to the needles is carried over the smaller glass and deposited there by disconnecting the current. A separation by dielectric means is, ordinarily, an unusually clean one, on account of a strong repulsive action to particles beyond the range of the liquid employed and a strong attractive action for those within the range.

It may be found necessary to alter the voltage in order to minimize *electric wind* effects, which make it impossible to collect material on the electrodes. The voltage must not be too low; otherwise the attraction or repulsion will not be observed.

If the mineral is found to possess a K of high value, the next procedure recommended is microchemical analysis. Unless the identification is complete, K should be determined for the resulting microcrystals. In order that this value may be of diagnostic value, it will be necessary to obtain a complete table of K for microcrystals made with chemically pure reagents. These values are best obtained by each investigator, in order that the conditions under which they are obtained will be identical with those under which unknown microcrystals are studied. The writer does not possess complete data in this connection, although experiments indicate a diagnostic value for the method.

A few K determinations on minerals are presented in the following Tables II and III.

TABLE II.—DIELECTRIC CONSTANTS OF MISCELLANEOUS MINERALS
(Highest value, $\lambda = \infty$)

Polybasite.....	$9(\text{Ag}, \text{Cu})_2\text{S.Sb}_2\text{S}_3$	>81 arc
Jamesonite.....	$2\text{PbS.Sb}_2\text{S}_3$	>81
Franklinite.....	$(\text{Zn}, \text{Fe}, \text{Mn})\text{O.}(\text{Fe}, \text{Mn})_2\text{O}_3$	>81
Stibnite.....	Sb_2S_3	>81
Rutile.....	TiO_2	>81
Pyrargyrite.....	$3\text{Ag}_2\text{S.Sb}_2\text{S}_3$	>81
Miargyrite.....	$\text{Ag}_2\text{S.Sb}_2\text{S}_3$	81
Stephanite.....	$5\text{Ag}_2\text{S.Sb}_2\text{S}_3$	<81 near
Plagionite.....	$5\text{PbS.4Sb}_2\text{S}_3$	>36 near
Boulangerite.....	$5\text{PbS.2Sb}_2\text{S}_3$	36
Manganotantalite.....	$(\text{Mn}, \text{Fe})\text{O.}(\text{Ta}, \text{Cb})_2\text{O}_2$	21.5
Dumortierite.....	$8\text{Al}_2\text{O}_3.\text{B}_2\text{O}_3.6\text{SiO}_2.\text{H}_2\text{O}$	17
Wulfenite.....	PbO.MoO_3	11.7
Vanadinite.....	$9\text{PbO.3V}_2\text{O}_5.\text{PbCl}_2$	10.8 — 11.2
Carnotite.....	$\text{K}_2\text{O.2UO}_3.\text{V}_2\text{O}_5.8 \pm \text{H}_2\text{O}$	9.3
Topaz.....	$2(\text{AlF})\text{O.SiO}_2$	8.8
Kyanite.....	$\text{Al}_2\text{O}_3.\text{SiO}_2$	8.8
Cuprodesclowitzite.....	$2\text{PbO.2CuO.V}_2\text{O}_5.\text{H}_2\text{C}$	8.6
Monazite.....	$(\text{Ce}, \text{La}, \text{Di})_2\text{O}_3.\text{P}_2\text{O}_5$	8.2
Scheelite.....	CaO.WO_3	7.7
Quartz.....	SiO_2	6.4

TABLE III.—DIELECTRIC CONSTANTS OF ZEOLITES
(Humidity, low. Temperature, 31°C. Highest value, $\lambda = \infty$)

Natrolite.....	$\text{Na}_2\text{O.Al}_2\text{O}_3.3\text{SiO}_2.2\text{H}_2\text{O}$	11
Analcite.....	$\text{Na}_2\text{O.Al}_2\text{O}_3.4\text{SiO}_2.2\text{H}_2\text{O}$	13
Crestmorite.....	$4\text{CaO.4SiO}_2.7\text{H}_2\text{O}$	17
Chabazite.....	$(\text{CaNa}_2)\text{O.Al}_2\text{O}_3.4\text{SiO}_2.6\text{H}_2\text{O}$	19
Stilbite.....	$(\text{CaNa}_2)\text{O.Al}_2\text{O}_3.6\text{SiO}_2.5\text{H}_2\text{O}$	22
Zeophyllite.....	$3\text{CaO.CaF}_2.3\text{SiO}_2.2\text{H}_2\text{O}$	25
Gmelinite.....	$(\text{CaNa}_2)\text{O.Al}_2\text{O}_3.4\text{SiO}_2.6\text{H}_2\text{O}$	>26

Fürth devised a very interesting method for the determination of K of good conductors. The substance is suspended in a liquid dielectric by a small fiber so that the rotational axis of the ellipsoid is horizontal. An electric field is generated between two plates which are separated a short distance. The field exerts a certain torsional moment to the substance whose K is to be determined, as the angle between the axis and the field direction differs from 0. In this arrangement, the greater the conducting power a substance possesses the greater is the frequency which must be used in the measurements.

Dielectric Constant and Molecular Structure.—The application of dielectric methods is not limited to mineral separation and mineral identification but is of great importance in the study of molecular structure. The following brief summary of the five principal methods of investigating the structure of the molecule has been given by Compton:

1. The ratio of the gaseous specific heat at constant pressure to that of constant volume on classical theory. This method is complicated by the fact that the energy is distributed according to quantum laws which approximate to the classical laws only in limiting cases, so that this method is of relatively little use.

2. The arrangement of atoms in crystals, as found by X-ray diffraction methods, gives a clue to the geometrical arrangement of atoms in molecules, since it is reasonable to assume that the particular atomic force fields which account for the arrangement of atoms in crystals are responsible also for their arrangement in molecules.

3. The molecular band spectra, as interpreted by the quantum theory. The distances between the atomic nuclei in a number of biatomic and triatomic molecules have been determined. Some information has been obtained regarding the degree of *firmness* with which these nuclei are held together.

4. Phenomena, such as molecular association, dissociation, ionization, and adsorption, indicate strong force fields around certain types of molecules, which presumably result from unsymmetrical arrangements of their electrical constituents. Typical molecules of this so-called *polar* class are H_2O , NH_3 , HCl , SO_2 , CH_3OH , while non-polar molecules are H_2 , O_2 , C_6H_6 , CO_2 .

5. Particularly significant are phenomena occurring when molecules, by being placed in an electric field, are distorted or oriented. Under this heading, we include refractivity and dielectric properties.

It is beyond the scope of this paper to enter into greater detail here. For further information, consult the paper by Compton.

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CHAPTER VI

GENETIC SIGNIFICANCE OF GRAIN

BY ALFRED C. LANE

1. The Production of Grains.—Above a certain temperature, atoms are fluid, having no fixed relation to each other. As the temperature drops, some of them group themselves together in molecules, while others remain dissociated in ionized groups. The condition is like that of people on a dance floor with occasional “stags” wandering about and “cutting in.” When the temperature drops to a certain level, crystals form about centers of crystallization, particles of impurity, the walls of a container, etc. In these crystals, the atoms are no longer like the moving, dancing couples; they are arranged in a fixed, regular network like sets in a quadrille, or lanciers, and held by electrochemical attractions. Frequently, there is one direction of greatest attraction, and then, if the crystals form rapidly, they are elongate in that direction, dendritic¹ or needle-like. Or there may be a direction of least attraction, in which case, they are flattened into tables or scales. Hematite and ilmenite often occur thus.

On the other hand, there may, as in isometric and rhombohedral crystals, be several equivalent directions (usually three) not in the same plane (the angles between are 60, $70\frac{1}{2}$ or 90 degrees in isometric crystals). This is the case in magnetite and galena. Then the crystals tend to be more equal in dimension.

In all cases, if the formation of the crystal is rapid, corners and edges tend to be more developed so that the faces between are concave or hopper shaped, and sections are forked, or we have dendritic forms. On the other hand, if the crystals form slowly, the corners and edges are rounded off, *modified*, and the dimensions become more nearly equal. Also, if the crystals form slowly, there will, in general, be fewer centers of crystallization

¹ PRIESTLEY, W. J., “Effect on Steel of Variations in Rate of Cooling in Ingot Molds,” *Trans. Am. Inst. Mining Met. Eng.*, No. 1,296-S, February, 1924.

and more room for them to grow and larger crystals. Tammann¹ distinguishes between the power of crystallization—the rapidity with which centers of crystallization come into being—and the velocity of crystallization—the rate of spread of the crystalline network from those centers.

As the temperature drops, more crystals form between the larger ones, and those which start first grow until all the material available is used or the temperature gets so low that the atoms are no longer free to move and arrange themselves to form crystals. This is the case in a glass. With a rapid enough drop and a low power of crystallization, there may be only glass. The more viscous the liquid the less the crystallization.

Thus, below the melting point there is a range of temperatures within which crystallization can take place. The mass is solid, but readjustment can go on atom by atom. It is the labile state, the annealing range, the *zone de revenus* of Girard.² The upper limit is the temperature of fusion (or condition of solutions). The lower limit is the *germinative temperature* of Jeffries.

Within this range, large crystals can grow at the expense of small ones, stable forms at the expense of metastable, and it

¹ TAMMANN, *Kristallisieren und schmelzen*. This subject has been worked on independently by Tammann and Doelter. Summaries given in *Neues Jahrb.*, 1903, Vol. I, and *Central Blatt*, 1903, p. 608. The power of crystallization is defined as the number of crystal granules forming in a unit volume in a unit of time. The velocity of crystallization is the linear velocity of growth in millimeters per minute. It seems to depend upon the number of degrees below the temperature of saturation, respectively fusion at which the crystallization takes place, or above the *germinative temperature* of Jeffries.

Pressure does not make much difference except as it may retain H₂O etc., but the crystallization is very sensitive to addition even of chemically neutral substances.

Glass formation may be due either to slow velocity of crystallization or weak power of crystallization.

During the first few degrees below saturation temperature, microlites and elongate forms tend to occur, later come the more equal-sized grains. In augite, the length of the grains formed in 100 minutes is not ten times that formed in 10 minutes, but Doelter's cylinder, which cooled in 100 minutes, had a slowly cooling margin and a more rapidly cooling center, a case we refer to.

² MATHEWSON, C. H., and A. PHILLIPS, "A Recrystallization of Cold-worked Alpha Brass on Annealing," *Trans. Am. Inst. Mining Met. Eng.*, p. 36, February, 1916.

seems, also,¹ that, other things being equal, as between curved boundaries growth takes place toward the direction of greater radius of curvature.²

The crystal-forming action is not solely loss of heat. It may be loss of pressure or diffusion of some constituent, as a gas which changes solubility. For instance, around lava bubbles there is a black zone of iron oxide (easily confused with weathering) which seems really due to loss of some *mineralizer* diffused into the bubbles. One may also see the same thing edging a crack in a basalt. The effect may be due to steam or air diffusing out or diffusing in. A similar effect of diffusion may be the flat tables of hematite and ilmenite near the center of a lava flow when granules down to dust, probably of magnetite, come near the margin. This occurs, for instance, in a dike from Kabberg (Kab Mountain) of the Bakony, which was sent me by Professor Von Szenpetery.

This may be due to a rapid diffusion of hydrogen in the margin whereas, near the center, it remains to react in accordance with the reaction



But in view of the fact that volcanic glass contains H and other reducing gases, this needs confirmation.

The diffusion of gases follows the same law as the diffusion of heat. This seems to be a general genetic law of fundamental importance.

The law is that the change in time at a given point is proportional to the acceleration of change in space. This holds true whether the change be one of temperature or of concentration. If the conditions are uniform all around a point, no change will take place there; and even if different, if on one side there is as much rise as on the other fall, what is lost in one direction will be gained from the other. There will still be no change in time. It is only when the drop on one side is more than the rise in the other that we get a change.

In general we may say: *The slower the crystal-producing action the coarser the crystal grains and the more nearly equal their dimensions.*

¹ COOK, M., and U. R. EVANS, "Recrystallization and Grain Growth in Soft Metals," *Trans. Am. Inst. Mining Met. Eng.*, No. 1,392-E, p. 3, November, 1924; LXXI, p. 627.

² MATHEWSON, C. H., and A. PHILLIPS, *op. cit.*

Thus, to put it more narrowly and precisely, the longer a body is held just below the crystallizing point, just above the germinative temperature, *i.e.*, in the *labile* zone, or the more slowly it passes through this zone the coarser the crystallization.

Rapid diffusion, therefore, promotes fine grain. For instance, metals conduct heat rapidly and, also, have great power of crystallization. Thus, a very fine-grained crystalline texture is easily attained.

Somewhere in the *labile* zone, probably near the top, the velocity of crystallization attains its maximum, and the power of crystallization, also, although not necessarily at quite the same point.¹

It is important from a genetic point of view to study the variation in grain relative to such surfaces, for such study may show whether the surface has the genetic importance attributed to it. For instance, the Sudbury² copper deposits of nickel, pyrrhotite, and chalcopyrite has been attributed to a magmatic segregation and crystallizing out of these ores at the base of a large sill of a magma. On the other hand, they have been attributed to later hydrochemical deposits.

A recent (1925) visit with Dr. H. V. Ellsworth and Dr. G. E. Marsh—to the Creighton Mine has convinced me of what I was not sure of when I visited the place with Barrell and others in 1913—that the norite sill is later than the Creighton Mine granite and has a variation of grain near its contact with the granite in which the ore body does not share yet that, however much segregation of the ore there may have been prior to the crystallization of the norite, the present ore body is subsequent thereto. It is *paulo post* for its grain is not dependent on the distance from the margin of the sill. It occurs in the country rocks (granite and older norite, etc.); the chalcopyrite occurs more on the joints.

¹ COOK, M., and U. R. EVANS, *op. cit.*, p. 20.

² Recent (1926) papers are by E. W. BAIN in the *Jour. Geol.*, Vol. XXXIII (1925), pp. 509-525; N. L. BOWEN, Vol. XXXII, p. 829; T. C. PHEMISTER, Vol. XXXII, p. 819, and the publications of the *Faraday Soc.* by J. W. GREGORY and T. C. PHEMISTER. The pioneers were A. P. COLEMAN, T. L. WALKER, MILLER and KNIGHT, and ROGERS. MILLER and KNIGHT's *Rept.* on the origin of the Sudbury nickel-copper ores. *Report* of the Ontario Nickel Commission, Vol. LXII, 1917, summarized the case to date.

One specimen of chalcopyrite shows a marked striation like that of plagioclase over an inch long, suggesting very slow formation.

It must be remembered that the diffusion of gas or the change of temperature from the surface is not necessarily a loss of temperature or other action promoting solidification. It may be, as in annealing, a rise in temperature into the annealing zone, in which case, Cook and Evans¹ find:

The temperature needed to produce appreciable change in a deformed metal is higher if the deformation is slight . . . if, however, the temperature is high the change will extend further into the regions of comparatively low deformation and . . . a zone of very large grains will be produced . . . The elevation may operate in two ways: (1) It will increase the number of nuclei formed in unit volume in unit time (Tammann's *Kernzahl* or K.Z.); this will tend to decrease the grain size; (2) It will tend to increase the velocity of crystallization (Tammann's *Kristallization-Geschwindigkeit* or K. G.) which . . . will clearly have the opposite effect. It is impossible to predict which of these two factors will prevail, in copper, brass, and tin a high annealing temperature usually causes a coarser grain.

Massing has shown that under certain conditions a high temperature may produce a smaller grain size in zinc . . . In aluminum, also, Carpenter and Elam have shown that under certain conditions a high annealing temperature causes a much finer grain . . . their well-known method of producing monocrystalline specimens consists in heating the specimens so slowly that the change is completed at the lowest temperature possible.

Jeffries cites numerous cases of . . . coarse grains when a piece of metal is heated to . . . the "germinative temperature," that is, the temperature just high enough to produce growth at a few (but only a few) points.

For hard metals, a comparatively high temperature is required; but for soft metals, in which the natural restraint on atomic movements is less, the rearrangement of atoms in stable crystal array occurs at a lower temperature.

We therefore divide our treatment into two parts according to whether or not the distance from a surface is significant. But first we shall discuss how the grain should be measured.

2. Measurement of Grain. (a) *Lane's Method.*²—Since the slower the diffusion from or to the surface the fewer will be

¹ COOK, M., and U. R. EVANS, *op. cit.*

² LANE, A. C., "The Keweenaw Series of Michigan," *Geol. Survey Mich.*, Pub. VI, Geol. Series, Vol. IV, 1911, p. 147.

the centers from which crystallization will start in a given time and, therefore, the fewer the grains which a section perpendicular to the direction of diffusion (and, hence, more or less parallel to that surface) will cut square through their middle.

I chose¹ the largest grains in a number of areas (microscopic fields). I took their average area, or the product of two dimensions, as representing the grain. Or, if I wanted the grain expressed in linear dimension, I took the square root of this product, or the average of the largest section of each grain.

*b. Jeffries' Method.*²—But in studying the grains of metals and alloys as Jeffries does, it is natural to consider all the grains, especially when they are all of the same kind.

We may, then, estimate the grain as he does, as so many per unit area. The reciprocal of this is the average area per grain. He counts the number of grains wholly enclosed by a circular field, adds 0.581 (or, in round number, 0.6) of the number of grains cut by the boundary of the field, and divides by the area of the field. If this is a microscopic field, of course the real area is apparent, divided by the square of the linear magnification, *e.g.*,

$$\frac{61 + 0.6^2 \times 35}{\pi(40)^2(100)^2} = 164.$$

The value for the denominator can be taken once for all. The average accuracy compared with the planimeter method is 2.4 per cent, sometimes greater, sometimes less.

c. Planimeter Method.—A more accurate method is to outline a certain number of grains and estimate by planimeter the actual area which they cover.

d. Heyn's Method.—Heyn took the average intercept along two sets of lines at right angles to each other. He then multiplied these two averages together to get the average area of the grain.

The method always gave more grains per square inch than the planimeter method. The average error is 13 per cent.

Hence, in comparing Heyn's method with Jeffries' observations, it would be well to increase by 10 per cent the area obtained by Heyn's method.

¹LANE, A. C., "Geology of Isle Royal," *Geol. Survey Mich.*, Vol. VI, Part 1, Chaps. IV, V.

²JEFFRIES and ZIMMER, "The Determination of Grain Size in Metals," *Trans. Am. Inst. Mining Met. Eng.*, February, 1916.

*e. Intercept Method.*¹—In this, readings are not confined to a set of parallel lines, but the average intercept along random lines is found and squared to get the area per grain. In this case, the average comes out 22 per cent less than the area by planimeter.

The mean of the squares is not the square of the mean and approaches it only when all the grains are of the same size.

f. Rosiwal Method.—This, used so much by petrographers, depends upon the ratio of the average intercept instead of the square of the intercept. It has been shown mathematically² that, under certain conditions, the volumes of two substances are proportional to the average intercept, not to the square thereof.

The question is, then, of interest whether it is better to measure grain by diameter, area or volume. The problem may be attacked by theory, or by observation and experiment, as shown below. The areas are more nearly proportional to the rate of cooling.³

*g. Relative Magnification.*⁴—I have experimented somewhat with an objective of varying magnifying power (3- to 5-inch focus). I compared the looks of a section, or rock, as a whole, with another at a different distance or differently magnified.

One can, also, in outdoor field work look at one specimen through a lens with one eye and bring another coarser specimen nearer or farther from the other eye until they match in coarseness and notice the distance from the eye. If, with a lens of 1-inch focus equal to about ten magnification, a diabase looks as coarse as a gabbro held 10 inches away, the latter is ten times as coarse as the former. If the latter must be held 20 inches away to match, it is twenty times as coarse. One can, thus, on the weathered edge of a diabase dike prove the rough applicability of the rule that near the edge the grain in linear dimensions varies as the distance from the margin.

3. Grain Not Varying with Distance from Margin.—In many cases, the change in conditions which produces crystallization is not closely associated with the distance from the margin. Let us consider some of these.

¹ MATHEWSON, C. H., and A. PHILLIPS, *op. cit.*

² LANE, A. C., *op. cit.*, p. 147, 1911.

³ LANE, A. C., "Geology of Isle Royal," *op. cit.* p. 126. "

⁴ LANE, A. C., "Grain of Rocks," *Bull. Geol. Soc. Am.*, Vol. VII, p. 406, 1896.

a. Clastic Grains in Stratified Rocks.—The grain size of the sedimentary rocks in which there has been an assorting action is due to wind or water.

The heavy and opaque minerals tend to occur in much smaller grains than the lighter quartz which is almost universally present. The soft minerals, unless they are in tough folia as is mica, are finer than the coarse, and the minerals harder than quartz, such as zircon, corundum, and diamond, retain traces of their crystal shape longer than quartz, while magnetite, ilmenite, and hematite round more rapidly, the rounding being inverse as the hardness.

The heavy grains, such as gold or cassiterite, tend to settle with the coarser grains of lighter minerals, such as quartz, and slip down into the crevices between the grains and, thus, aided by microscopic earthquake shocks, work their way toward the bottom of the bed.

The farther from the source the fewer and rounder are the grains. Wind rounds down to a smaller size than water (0.3 millimeter).

Ice-transported material—till *i.e.* boulder clay and tillite—is not so rounded or assorted, and material transported by the ice with a brief handling by the waters of the melting ice may have the clay removed with but little handling of the gravel. Grains so fine as to be transported by flotation may be practically unrounded though handled a long way.

Ash fragments which settle from a volcanic-dust explosion are often conchoidal fragments of glass.

b. Granulation by Deformation and Crushing.—Again, we have the grain size produced by granulation through crushing and the deformation and working of metals.¹

The fragmentation of a solid rock through crushing comes in mylonites and metamorphic rocks, giving angular fragments of all sizes.

We also have the flow of a plastic or viscous mass. This gives us the protoclastic texture and the brecciated structure of certain rhyolites. A characteristic feature is often the mortar structure, a granulated zone or margin surrounding larger areas, a very uneven grain of the same mineral. We have this, also, in the "augen gneiss."

¹ COOK, M., and U. R. EVANS, *op. cit.*

The grain of the crushed-quartz flour at the bottom of Meteor Crater,¹ a dent made by the impact of a big meteor, should be mentioned as a freak.

c. Colloid Precipitation.—We have immediate crystallization from the mixture of two solutions, just as I once saw a drill rope dyed intensely black from going through a stratum containing a chalybeate water with iron bicarbonate and then, farther down, striking a water containing sulphuretted hydrogen precipitating iron sulphide.

In such cases, the precipitation may be so rapid as to form colloids with the characteristic botryoidal appearance.² Their original grain is ultramicroscopically fine.

On the other hand, if this mixture of two solutions is slowed up by diffusion in a viscous or somewhat impervious medium, such as mud, the resultant crystals, such as the crystals of pyrite which occur at times in shales or gypsum, may be very large and perfect. Their size is, then, fixed by the rate of diffusion and the difference of conditions. In other words, the grain is fixed by conditions described below.

A colloid held in or raised to the labile (annealing) state will pass into the crystalline condition (chalcedony turning into a fine-grain quartz mosaic, obsidian into felsite).

The coarseness of the grain may depend on how far it gets into the annealing zone.³

d. Schisto-recrystallization under Differential Pressure.—A mass of rocks, being metamorphosed by deep burial and increasing pressure, will have its constituents recrystallized into more compact networks, as Van Hise and Leith have emphasized.

As F. E. Wright experimentally pointed out,⁴ crystals which form in glass, or other medium under differential pressure, form with their greatest atomic density, their cleavages, and elongation as nearly as possible at right angles to the direction of pressure. Thus, we have the parallel structure of the schists

¹ Barringer, Meteor Crater, 1909, further notes on Meteor Crater, 1924. See, also, papers by Elihu THOMSON, *Proc. Am. Acad. Arts Sci.* Vol. XLVII, p. 71, 1912; various papers in the *Bull. Geol. Soc. Am.* by W. C. LEE, and H. L. FAIRCHILD, Vol. XVIII pp. 221, 496-499, 1907; other papers by J. C. BRANDON, H. L. GILBERT, and G. P. MERRILL.

² MATHEWSON, C. H., and A. PHILLIPS, *op. cit.*

³ COOK, M., and U. R. EVANS, *op. cit.*

⁴ WRIGHT, F. E., "Schistosity by Crystallization," *Am. Jour. Sci.*, Vol. II, pp. 224-226, 1906.

specular (hematite); also mica, chlorite and talc and graphite and hornblende schist, etc.

e. Recrystallization into Stable Forms.—Deep burial means an increase not only of pressure but also of temperature. We have, then, two combined factors tending to promote recrystallization into more stable forms under such conditions. For instance, hornblende may be more stable than pyroxene, and glass is certainly unstable and tends to change to felsite (quartz-feldspar fine-grained mosaic). Chalcedony or opal tends to change to cryptocrystalline quartz, and many colloids to become more coarsely crystalline.

f. Porphyroblasts (Metacrystals).—In the process of metamorphism, the rock may be so softened that it has no longer differential pressure but the pressure becomes practically hydrostatic.

The quartz moisture which may remain will be highly solvent. As it very slowly comes back to surface conditions, crystals may form very slowly and, therefore, extraordinarily large. This is the characteristic mode of occurrence of staurolite, chloritoid, and chiasolite. Ilmenite also, may, occur in this shape. The crystals are built out in all directions in their own forms but may enclose earlier material in amoeboid fashion.

g. Solution under Pressure Relief—Brotocrysts.—Relief of pressure and change of temperature with or without diffusion and apart from metamorphism and moisture change equilibrium and may promote solution and recrystallization. In fact, Bowen has called attention to the fact that the crystallization of olivine to be dissolved later and used for the building of pyroxene may be a normal point of the development of a magma. Corroded remnants of such larger crystals are a kind of phenocryst (porphyritic crystal) that I have called *brotocrysts*.¹

But it is also true that the magma or melt may crystallize under a pressure which promotes the retention of mineralizer. Or eruption may take place, and the viscous movement of the melted magma may generate heat. Under new conditions, earlier crystals may be dissolved, new ones formed.

h. Crystallization during Later Stages of Diffusion.—In all cases above mentioned, except the sedimentary clastic grains,

¹ LANE, A. C., "Studies of the Grain of Igneous Intrusives; Porphyritic Appearance of Rocks," *Bull. Geol. Soc. Am.*, Vol. XIV, pp. 369-407, 1903.

I think it is safe to infer that the coarser the crystallization is the slower was the formation. In the huge masses which are found of native copper, amounting to many tons, I have been informed by W. J. Uren that patches as much as $1\frac{1}{2}$ feet across have been proved by etching to belong to one crystal. In the same way, the Widmanstättian figures on the iron of meteorites indicate that it crystallized slowly.

I am inclined to think that this holds true and has genetic significance as applied also to nodules, geodes, septaria, and spherulites. Spherulites are, to be sure, a structure due to a rather rapid devitrification and change to a more stable state from relatively few centers, the power of crystallization being low relatively to the velocity of crystallization. I have made them in barley candy, and they form in glass at the annealing temperature, but their size may indicate how rapidly descent was made through the annealing stage, labile state and may be a function of distances from surface as well as of slight variations in percentage of mineralizers.

4. Grain as a Function of Distance from Margin. (*a*) *Laws of Dependence.*—As has been said, the slower the diffusion from or to the surface the fewer will be the centers from which the crystallization will start in a given time and, therefore, the fewer the grains which a section parallel to that surface (or, more strictly, as discussed by B. O. Pierce before the American Academy of Arts and Sciences,¹ normal to the directions of diffusion) will cut through the middle. This agrees with the results of Cook and Evans.² If we consider that the time t and the distance from the margin x are the only variables to be considered, whether the diffusion be of gas or caloric to or from the margin, then it is not hard to believe, as above, that the change in condition at a given distance from the margin should be proportional to the change in the rate of variation of condition in space; because, if the rate of change of condition is the same on both sides of the point, it will gain from one direction what it loses in the other, and its own condition will not change.

If this be true, then it has been shown for a wide range in conditions (by B. O. Peirce, Kelvin, R. S. Woodward, Lane

¹ PEIRCE, B. O., *Proc. Am. Acad. Arts Sci.*, Vol. XXXIV, p. 1, 1898; Vol. XXXVI, pp. 11–16, 1900; Vol. XXXVIII, p. 649, 1902; Vol. XLV, p. 340, 1909. HAYES, H. C., Vol. XLVII, pp. 1–6, 1911.

² COOK, M., and U. R. EVANS, *op. cit.*

Ingersoll, Zobel, Adams, Williams, and others)¹ that the percentage of change from initial conditions (u/u_0) is a function of $x/2\sqrt{at}$, where a^2 depends on the rate of diffusion for the particular mass concerned. Obviously, then, the conditions will be the same at twice the distance from the margin in four times the time. If, then, the grain is proportional to the distance, it is as the square root of the time if measured in linear dimensions. As a matter of fact, this is true near the margin of many dikes and flows and melts, where the margin is at a constant temperature or may be supposed to be so kept by melting ice or evaporating water.

The grain measured in areas will then be as the slowness of cooling.

As it often represents sufficiently well the facts, and as the more complicated case may be made dependent on it, we treat, first, the case where the contact surface or margin is kept under constant conditions.

b. Conditions at Margin Constant.—In this case, the change in conditions is expressed by a series of curves which may be expressed in series in two ways.² Early stages in cooling are expressed well enough by the first term only of the first way. Later stages of cooling are well enough expressed by the first term of the second mode of expression. This is true as soon as (u/u_0) is less than three-fourths and is true if there is any central belt of uniform grain. If there is any such belt, let us call its linear grain E and we have

$$E = \frac{kc}{\pi a \sqrt{u}}.$$

That is, the grain is proportional to the power of crystallization k and to the thickness of the sheet c but inversely proportional to the square root of the diffusivity a and to the difference in initial conditions between the sheet and margin u .

At early stages of cooling, during which the increase of grain is at the distance from the margin (x), the first term of the first

¹ INGERSOLL, L. R., and O. J. ZOBEL, "Introduction to Mathematical Theory of Heat Conditions." Various papers published by the Geophysical Laboratory, Washington, District of Columbia, by N. L. BOWEN, ADAMS, and WILLIAMSON. See, also, LANE, *op. cit.*

² LANE, A. C., "The Keweenaw Series of Michigan," *Geol. Survey Mich.* Pub. VI, Chap. IV, 1911, p. 156 etc. See also "Studies of the Grain of Igneous Intrusives: Porphyritic Appearance of Rocks," *Bull. Geol. Soc. Am.*, Vol. XIV, 1903; p. 391 contains a misprint which is corrected in Pub. 6 on p. 159.

series, given below, sufficiently expresses the ratio (u/u_0) . In that case, the grain may be expressed thus:

$$g = \frac{x}{c} \cdot \frac{kc}{a\sqrt{u_0}} \cdot \frac{1}{h\sqrt{2(u/u_0)^3}}.$$

The term h is, in general, a very complicated function (see Fig. 3) but practically as long as (u/u_0) is less than 0.9 it varies only between 0.8 and 0.88 and near the margin is not a function of x but solely of (u/u_0) . Thus, if we let the rate of increase at the contact or margin be C ,

$$g = Cx = \frac{ku_0x}{ah\sqrt{2u^3}} = \frac{k/u_0x}{1.26a\sqrt{u^3}}.$$

We see that it is like E in being greater the greater the power of crystallization and the less the diffusivity, but in distinction therefrom it does not depend on the size of the sheet. This is natural, since it is crystallization before the center has cooled off to speak of. If it had not cooled off at all, it obviously would make no difference how much more there might be back of it. It, also, does depend on the difference in conditions between the magma or melt and the country rock.

The breadth of this zone of increasing grain may be taken as, roughly, the breadth where the increase of grain would give the grain at the center if it kept up, *i.e.*, where g would equal E , *i.e.*, x would be $E/C = chu\sqrt{2/\pi u_0} = \text{about } 0.4c(u/u_0)$.

It is, then, nearly proportional to the size of the dike and the degree of superfusion as is illustrated by Figure 1.

This is obviously a very important genetic factor.

It must be remembered that a high superfusion probably quite as often comes from a high country-rock temperature as from any excess temperature of the magma, for u and u_0 are both measured from the conditions of the surrounding medium, so that if that is raised but the initial conditions of the magma and of the labile zone remain the same, the ratio of u to u_0 becomes less, and the grain coarser everywhere.

If the consolidation so immediately follows the intrusion that u/u_0 is more than 0.9, then, at the center where $x = c/2$, the grain will be greater than that given by the formula for E and will approach $g = Cc/2 = kcu_0/ah\sqrt{2u^3}$, which is less than $kcu_0/0.63a\sqrt{u^3}$.

From some observations on the iron ore of lavas and diabases of the Keweenaw series and similar rocks, I estimate that C

is about .000006 (6 millimeters in 100 meters, if it is kept up. It is very likely, however, to show resorption and, with the olivine, to be redissolved to form pyroxene). If the marginal increase of grain did hold clear to the center, it could be only because the crystallization all took place before the center had cooled and the

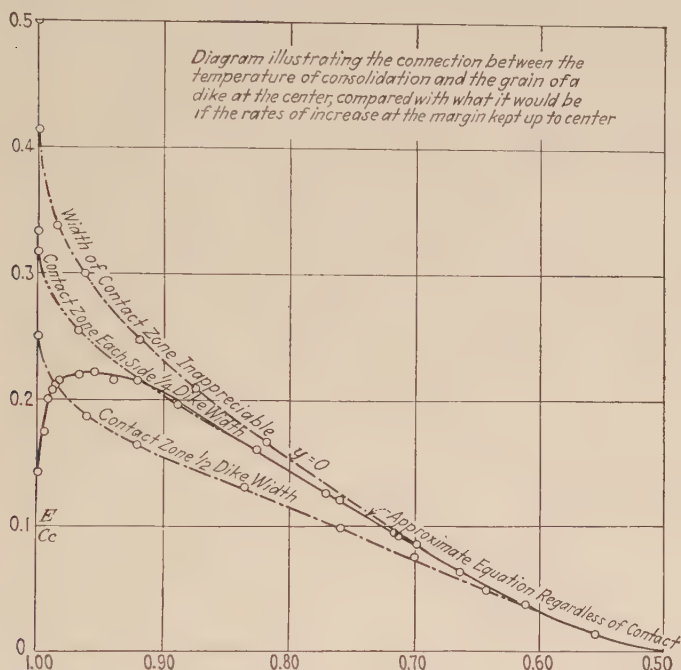


FIG. 1.—Shows by its abscissas the relation of the consolidation temperature (or labile zone) to the initial temperatures of molten sheet and its country rock, beginning on the left with the halfway point. The ordinates show the consequent ratio of the grain of a central zone of uniform grain, if present, to what the grain would be if the rate of increase kept up for full thickness, and hence approximately the width of a zone of finer grain near the margin to the whole width.

The dot and dash curves show the result, making allowances for various breadths of contact while the full curve is plotted from a formula which is approximate up to about a nine-tenths of the initial (u_0). (After Fig. 21 of Publication 6, Michigan Geological and Biological Survey.)

labile zone was that of the initial conditions. This is true of the pyroxene of some surface flows.¹

Naturally, we should expect to find, and we do find, that in surface lavas the labile zone is relatively high. For, first, flow stirring and convection may easily last until the lava begins to stiffen; secondly, the labile zone may be raised by loss of gases;

¹ LANE, A. C., *op. cit.*, 1911.

and, thirdly, and most important, the country rock is more likely to be colder and wet- and heat-absorbent.

In the dikes, the heating up of the contact plays more role, and in the abyssal rocks it is still more important. We turn to this problem.

c. Margin Conditions Not Constant.—When we allow for a heating up of a contact zone after the lava is intruded, it may be found, from the solution of the case, that the walls or margin are kept in constant temperature or condition in the following way (we shall take temperature for illustration):

Assume the appreciable alteration of temperature or other conditions to be confined to a zone AD of width c , in the center the cooling sheet BC of width $2w$ intruded at the temperature u . Suppose the diffusivity (a^2) to be constant throughout. Then the temperature of any point P of the zone affected within BC

$$\frac{A \quad B \quad P \quad C \quad D}{P_1 \quad P_2}$$

FIG. 2.—Illustrates the relation of the point P in a dike with the section BC and contacts zones AB and CD to the points P_1 and P_2 in a dike with width CD and walls at constant temperature, from which its temperatures can be computed.

is easily derived as the average of those of two points P_1 and P_2 in a sheet of width equal to the whole width c and with the same initial temperature and diffusivity, whose margins are kept without change at the same temperature as the contact zone originally had. If P is outside BC in the contact zone its temperature will be half the difference of the temperatures of P_1 and P_2 . These two points are as far from A and D , respectively, as P from B and C . Thus, the solution of this case may be made to depend on the simpler case we have already described.

In my Isle Royale report,¹ I give a formula for the case in which the contact zones are not symmetrical.

In case the diffusivity is not the same but is uniform in the contact zones, they may be replaced for the mathematical formulas by ones in which is an equivalent resistance to heat but which have a different thickness, and the diffusivity of the central sheet. Only note that if the contact country rock or

¹ LANE, A. C., "Geology of Isle Royal," *Geol. Survey Mich.*, Vol. VI, Part 1, p. 117, Eq. 9.

mold has a high diffusivity, as in the case of Priestley's¹ cast-iron molds, the actual contact zones in their effect on cooling are equivalent to less contact zones of the diffusivity of the melt, since their outside is supposed to be kept without rise of temperature. The greater the diffusion the less these zones get, until, if the diffusion were infinite, we should gradually pass into the case already studied.

In the case where the diffusivity is very low, we may then replace them mathematically by larger contact zones. Contact rocks of varying diffusivity may have marked effects on the marginal grain of the intruding rock.

(1) Contact Zone Small.—In the case of small contact zones illustrated on p. 380 of my report of 1903, the margin starts at a temperature halfway between the conditions inside and outside, *i.e.*, at $u_0/2$. It soon drops and, before the center has cooled materially, is cooling as though the cooling originally started at the outside of the contact zone. We can distinguish theoretically, and sometimes practically, two belts of linear increase of grain, one before the margin has cooled at all, and another when the cooling is as though it had started in a sheet the full width of the sheet and contact zones.

In the first case, the cooling is as though it were in a sheet of the size and thickness of the molten sheet, with its margins held at the temperature u_0 . Thus, the interval of cooling will be from u_0 down through u to $u_0/2$. Thus, for (u/u_0) we must write $(u - u_0/2)/u_0/2 = (2u/u_0 - 1)$. We must figure the distance from the edge of the dike.

This is much greater than the ratio and increase which would be obtained by supposing the contact zone to keep chilled; for u/u_0 is less than one, hence, $(2u/u_0 - 1) = (u/u_0) - (1 - u/u_0)$ is less than u/u_0 . As it comes in the denominator, the fraction is greater.

In the Keweenawan basaltic rocks, it seems to be confined to only the first foot or so; and for magnetite, the rate may be 0.0002; for the Kab Mountain basalt, 0.0002.

The second belt of increase (which, as the contact zone gets smaller or the labile zone relatively higher, becomes more and more important) is when the molten sheet and the contact zones are cooling as one.

¹ PRIESTLY, W. J., *Trans. A. I. M. E.*, LXX, 73.

In this case, the grain follows a straight-line curve

$$g'' = Ax' + B = \frac{kc}{au_0} \times \frac{1}{ch' \sqrt{\left(\frac{u}{u_0}\right)^3 - 2}} \times \left(\frac{c - 2y - 2y'}{c - 2y} x' + y' \right).$$

In this formula, h' and C refer to values for the reference sheet, y represents the thickness of the contact zone, and y' is connected with y by the formula

$$\sin \frac{\pi y'}{c} = \frac{1}{2} \sin \frac{2\pi y}{c}$$

This is an important rate of increase in the Keweenaw flows and dikes and, unless the contact zones are large, is, as C is practically independent of the size of the flow or dike.

In the Keweenaw flows, it seems to be about 0.00006 to 0.00008. In all cases, if the contact zone is small, there is a flattening of the curve of grain, a region of least curvature, corresponding to this rate which corresponds to the time after the contact zone has heated up so as to cool down with the rest of the zone disturbed by the molten matter as one piece. It does not point to a marginal grain or zero at the present margin, and thereby an estimate of the marginal zone may be made from B/A of the equation above.

If there is a belt of uniform grain inside it, the width of the zone from the outside of the contact zone to the zone of increasing grain is, as before, approximately $0.45(u - u_0)hc$, where h includes the effect of the contact zones of disturbed temperatures. For instance, if u/u_0 is 0.8427 and is $P_{x/2a}\sqrt{t}$, the zone of increasing grain is $0.32c$. This is about the limit when there is any belt of uniform grain at all.

(2) Contact Zone Large.—(Fig. 3.) If the contact zone is large, the middle zone of increasing grain drops out; the margin remains at halfway temperatures until after the center has cooled down. The formulas for the marginal and central grain remain unchanged, when the labile zone is above that of the marginal temperature.

If the labile zone is less than this, the grain will be coarser at the margin than at the center. This feature becomes less marked the lower the labile or crystallization zone is, and, not much below, the grain will be uniform throughout from one side to the other. This is the characteristic grain of aplites—small dikes in a yet hot granite.

On the other hand, if the crystallization is only slightly higher than the margin initial temperature, it is fine grained at the margin, but there is a coarser belt between it and the center belt of uniform grain. The higher the conditions of crystallization are—the nearer to the initial conditions of the magma

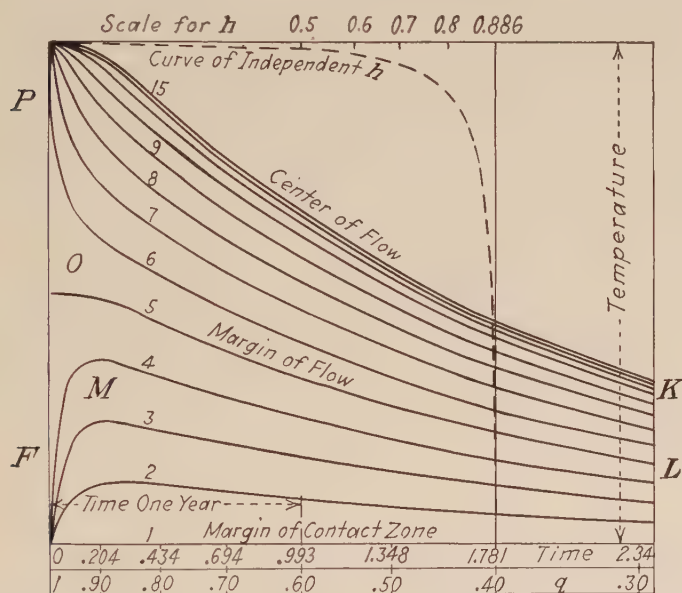


FIG. 3.—Illustrates the cooling, and hence by the slopes of the cooling curves the grain, of a dike which has a contact zone one-fourth of the width on each side. The heating up of the contact zone is also shown. The abscissas represent time, the ordinates, temperatures and the curves represent the cooling for twelve points equally spaced from the margin of the contact zone to the center.

There is also given by dashes a curve showing the value of h which is

$$h = \sqrt{\frac{-dm/m^3}{-d(u/u_0)/(u/u_0)^3}}$$

when it is a function of u/u_0 only, i.e. for early times. See appendix at the end of the chapter. (After Fig. 18 of Publication 8, Michigan Geological and Biological Survey.)

(as $u = u_0$)—the less and the farther in is this coarser belt, until, somewhere about $u = 0.6u_0$, it ceases. From there up, we have simply a marginal belt of rapidly increasing grain, comparable with C and not A , and with a short easement curve the belt of uniform grain, less and coarser the greater u is. This may be of value in comparing the relative order of formation of certain minerals. Bowen¹ has called attention to the fact

¹ BOWEN, N. L., "The Later Stages of the Evolution of Igneous Rocks," *Jour. Geol.*, supplement to Vol. XXIII, No. 8, pp. 8-29.

that some of the criteria of age show the relative ending, others the relative beginning, of certain minerals. This test might give the mean order.

5. Genetic Applications.—It will be noticed with regard to all these formulas, that the less the difference of conditions between the magma, or melt, and the country rock, or mold, the coarser will be the grain.

This is particularly true when the country rock is not far from the labile zone. Moreover a lack of dependence of the grain upon a particular contact shows either that that contact had nothing to do with the crystallization or that the conditions of crystallization were much nearer to those that already prevailed in the country rock, that in other words the country rock was relatively near melting or dissolving.

This may be applied in comparing the genetic order of pegmatites and aplites. If belonging to one eruptive period, the coarser grain of the former show that they are later, when the country rock or mold was much nearer the conditions of their crystallization than was the case in the aplites.

We see, thus, how the grain may give us light on the genetic relations of the labile zone.

We have noted that the relative position of the labile zone may be shifted in three ways: by relatively lower initial temperature of the magma, or melt, by relatively higher temperature of country rock, or mold, and by the differences in the conditions of crystallization, mineralizers, etc., of the various minerals. All these possibilities must be kept in mind. The early formed brotoocrysts and phenocrysts throw some light on the upper temperature. Orthoclase is decomposed at 1170°C., etc.

An extreme variation with slight differences in conditions when the crystallization is about halfway between the initial conditions of the magma or melt and the country rock or mold comes not infrequently in igneous rocks and is significant.

Assume for a gabbro, a rock which often has a grain for the pyroxene which suggests that the initial temperature made u/u_0 very little above 0.59, that the country rock had a temperature of 100°C. The crystallization of the pyroxene was probably below 1000°C. and not below 800°C. Then, we have 1500 to 1800° as the initial temperature of the gabbro, which, at 3° per 100 meters, means that it came, not allowing for heating effect of friction, from 50 to 80 kilometers down.

Phenocrysts of feldspar show that granite while yet in motion was not above 1170°C. Quartz of granite type crystallizes presumably between 600 and 800°, and the well-marked finer marginal grain in granites is quite reasonable. *A uniform grain suggests a high country rock temperature.* I use these petrographic illustrations because the application to opaque sections is practically a virgin field.

The determination of four things— \sqrt{C} , A , B , E ,—as to the grain by observations will, if the other quantities entering into the equation, the power of crystallization, etc., are by experiment known, gives, us the four things about a particular sheet and particular mineral, for instance, the width of the contact zone, the initial, country-rock and crystallization temperatures.

Appendix

The mathematical equations for the cooling of a sheet with constant wall temperature (0°), initial temperature (u_0), and diffusivity (a^2) are (Ref. 8. Lane, loc. cit. p. 157).

$$\frac{u}{u_0} = P_m - (P_{(m_0 + m)} - P_{(m_0 - m)}) + (P_{(2m_0 + m)} - P_{(2m_0 - m)})$$

$$m = \frac{x}{2a}\sqrt{t}; m_0 = \frac{c}{2a}\sqrt{t}; P_m = \frac{2}{\sqrt{\pi}} \int_0^{m_\epsilon - m^2} \frac{c}{m}$$

$$\frac{\pi}{4} \frac{u}{u_0} = q \sin \frac{\pi x}{c} + q^9 \sin \frac{3\pi x}{c} + q^{25} \sin \frac{5\pi x}{c}$$

where $\text{nat log } q = -\pi a^2 c^{-2} t$.

CHAPTER VII

ORE-MINERAL SEQUENCE

BY R. J. COLONY

Mineralization phenomena are the result of previous preparation usually connected with certain dynamic conditions which pave the way for the subsequent, but closely following, deposition of the ore minerals.

The complete operation of these processes, from the inception of the first movement productive of deformation, through the deposition of gangue minerals, to the final crystallization of the last hypogene ore minerals, may be called a *mineralization epoch*. A single mineralization epoch may be considered as having been completed *without interruption*, except, possibly, some resurgence of intensity or slight renewal of deformation toward the close of the period, when it is productive of mineralization which does not imply a second, remote, and totally distinct epoch, although it may overlap more or less.

For the purposes of interpretation, a mineralization epoch may be divided conveniently into (a) sequence of events and (b) sequence of minerals (*paragenesis*). The interpretation of the *sequence of events* involves a thorough petrographic study of properly selected material, including not only vein or ore-zone samples but wall rock and country rock as well, with whatever other associated rocks of igneous or other origin may have a bearing on the problem. Since an explanation of this phase of the general mineralization problem is beyond the scope of a discussion of ore-mineral sequence, it will suffice to indicate, in a very general way, the method of attack.

Sequence of Events.—The *sequence of events* is the historical phase of the mineralization epoch; it is determined by an interpretation of the stages which resulted from the operation of the different processes, from the inception of the epoch to its conclusion. The criteria are largely structural but are also, in part, mineralogical. Thin sections, cut from an especially selected and complete suite of rock and ore samples, form a necessary

adjunct to the petrographic study; the proper interpretation of these helps to determine the historical part of the mineralization epoch.

More than one epoch may be represented, separated by a *deformation unconformity* and by a lapse of geologic time. Thus, two distinct epochs (Epoch I and Epoch II), each complete in itself, may be separated sharply by (a) a series of products of totally different type and of different composition, commonly formed under quite different physical-chemical conditions; (b) veinlets cutting all of the members of Epoch I, filled with gangue and ore minerals of totally different character, belonging to Epoch II; (c) a series of Epoch I minerals more or less modified by the processes which were operative in the production of the minerals of Epoch II; and since the minerals of Epoch II were in equilibrium with the temperature-pressure-concentration conditions under which they were produced, they should not themselves be modified except by still later processes—processes which would be connected with a third and different epoch (Epoch III).

As an example of Epoch III may be mentioned supergene attack on minerals of epochs I and II, with possible enrichment effects. The minerals of each epoch have a special sequence of their own. When two distinct and different epochs are recorded in the ore, and the same mineral, among others, has been formed as a result of the processes operating during each epoch, some confusion in the interpretation of both sequence and ores may arise. For example, an ore carrying bornite and chalcocite of hypogene origin, and belonging to the first mineralization epoch, may have been subjected to oxidizing conditions with the formation of supergene chalcocite in Epoch II, so that chalcocite of two different origins, each belonging to a totally different mineralization epoch and of vastly different significance in interpretation, may be mixed in the same ore.

Other structural conditions simulating two separate mineralization epochs should be guarded against in the interpretation of *sequence of events*. For example, a quartz-vein sample may exhibit shear and crush zones healed with quartz; with the later quartz is associated valuable ore minerals. This structural condition does not necessarily imply two separate and distinct mineralization epochs, separated by a deformation unconformity. On the contrary, the shearing of the quartz frequently occurs by

reason of a slight renewal of deformation during the closing stages of the mineralizing period of the epoch, all of the mineralization being accomplished during a single epoch. Accordingly, both earlier and relatively later quartz belong to the same mineralization stage, the later quartz filling weaknesses in the earlier, being merely the concentration residuum of the quartz *solution* itself and carrying as concentration residua the associated valuable ore minerals.

Sequence of Ore Minerals.—In polished plates of opaque ore minerals, the sequence of deposition is determined almost wholly by the marginal relations of the different grains to one another and by cross-cutting structures, such as veinlets and filled fractures, and to certain other structures and conditions mentioned below. To considerably less degree, the minerals themselves offer, at times, information which is suggestive in connection with the structure criteria.

The marginal relations, or contacts, between the different minerals, are, in general, of two kinds: (a) smooth, either straight or curving; and (b) jagged, or penetrating.

Certain special structures and mineral associations, although considered here separately for convenience, may be properly assigned to either group, dependent on the type of mutual boundaries presented by the grains which collectively form the structure. These structures embrace

1. Graphic structures and intergrowths.
2. Concentric structures.
3. Banded structures.
4. Cores of ore minerals, surrounded by envelopes of a different mineral or of different composition.
5. Inclusions of one or more minerals in another, oriented or not.
6. Embayments, corrosion effects, pseudomorphs, and cross-cutting structures, such as veinlets and reticulate structures.
7. Association incongruity.

Marginal Relations.—(a) Smooth contacts, either straight or curving, between the various grains of ore minerals, usually imply contemporaneous deposition. Some minerals appear to possess a stronger *crystallizing force* than others, and these have a tendency to appear in crystal form, even when they are in contact with, and surrounded by, other minerals which were deposited simultaneously. Pyrite and arsenopyrite characteris-

tically behave in this way. Galena and sphalerite occasionally may present the same aspect, although sphalerite occurs much less commonly in crystal form, especially when contemporaneously intergrown with its common associates, pyrite and galena. An example of smooth curving margins and smooth straight margins, as well, conditioned by the contemporaneous deposition of galena and tetrahedrite, is shown in Fig. 1. Galena, with characteristic triangular cleavage pits, is in contact with tetrahedrite; the boundaries between the two minerals are such as to suggest essentially contemporaneous deposition. The

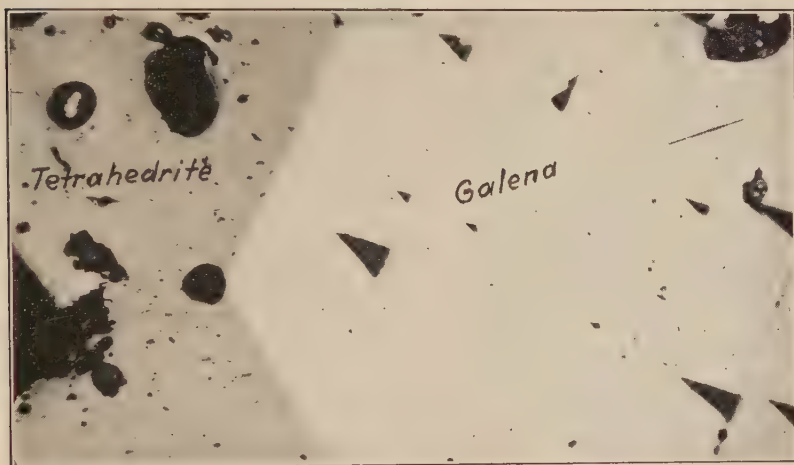


FIG. 1.—Illustrating smooth boundaries. X85.

Galena, with characteristic triangular cleavage pits, in sharply straight, smooth contacts on two sides with tetrahedrite. A third side exhibits smooth, curving marginal contact with the tetrahedrite. Such mutual boundaries are usually evidence of contemporaneous deposition and hence may be taken as one of the criteria for contemporaneity.

tetrahedrite deposition continued, perhaps, a little longer than the time of deposition of the galena, so that there is, in places, slight encroachment by the tetrahedrite; nevertheless, the two minerals may be regarded as contemporaneous deposition products. In most cases, ore minerals of contemporaneous deposition, in contact with one another, do not exhibit sharp straight boundaries due to the development of crystal faces; they are distributed in allotriomorphic grains whose mutual boundaries are smooth and curving. Smooth marginal contacts, either straight, curving, or gently crenulated, may be considered good criteria for contemporaneous deposition, provided the possibility of pseudomorphous replacement be kept in mind.

(b) When the contacts between the different ore minerals are sharply jagged, and when splintery and penetrating structures are prominent, there is suggested encroachment or attack by one component on another, marking a sequence in deposition. It is sometimes difficult to determine, however, from the marginal relations alone, which mineral is the earlier, since either one seems to penetrate or encroach on the other. In such cases, some additional relationship is necessary to determine which



FIG. 2.—Illustrating jagged, splintery forms. Pyrite and sphalerite. $\times 300$.

In this polished plate most of the pyrite is idiomorphic, whether in contact with the sphalerite or not; that is, the pyrite is distributed in individual, well-formed crystals, with straight, smooth boundaries in contact with the sphalerite; hence, by such criterion, pyrite and sphalerite are contemporaneous in this ore. Here, however, there is some evidence of slight encroachment on the pyrite by the sphalerite.

of the two minerals is the earlier. Structures indicating corrosion or marginal replacement usually are the best supporting evidence.

In Fig. 2, sphalerite is shown encroaching on pyrite, although through the larger part of the polished plate the pyrite exhibits straight smooth boundaries against the sphalerite. In both the cases illustrated, contemporaneous deposition may be inferred; but in one of the ores tetrahedrite was deposited during a slightly longer interval of time than was the pyrite, and, hence, during

the closing stages of the tetrahedrite deposition it was capable of encroaching slightly on the codeposited pyrite. The same explanation may be given for the structures shown in Fig. 2, where sphalerite encroaches slightly on the pyrite.

If one has to depend wholly on jagged boundaries and splintery, penetrating structures, it is not always possible to determine which of the two minerals thus in contact is the earlier. In Fig. 5, for example, it would be difficult to tell whether the covellite or the chalcocite was the earlier of the two minerals, since each penetrates the other. There is, however, a supporting criterion in the form of corrosion effects. In places, the covellite has been corroded by the chalcocite, and, therefore, the chalcocite may be judged to be later than the covellite.

Replacement remnants of bornite in the chalcocite furnish additional evidence of sequence and suggest, likewise, the possibility of two separate mineralization epochs, although there is no positive proof of this. The evidence for replacement of the bornite is based on the extremely ragged, strongly crenulated margin of the bornite and the fact that the embayed remnants are included wholly within the chalcocite. On the evidence presented by the structures mentioned and illustrated in Fig. 5, the chalcocite is judged to have encroached on both covellite and bornite and, thus, is later than either. Hence, the sequence would be (1) bornite, (2) covellite, (3) chalcocite. Moreover, the possibility is suggested that the bornite belongs to mineralization Epoch I, whereas chalcocite was developed during mineralization Epoch II.

Other Special Structures.—Contemporaneity and diversity in age may sometimes be determined from the various structures developed during the deposition of the different ore minerals. The more significant of these are

1. *Graphic Structures.*—Much has been written on the subject of graphic structures and their significance and interpretation.¹ The consensus of opinion favors a replacement origin (hence, sequence) for them, but a question arises as to the *original* structure, that is, whether selective replacement of one component of an intergrowth that was *itself* original (hence, contemporaneous) produced the graphic structure, or whether a highly

¹ All references to the bibliography of graphic structures and of sequence have been omitted. The writer acknowledges his obligations to the many who have published their observations on these topics.

selective attack on an original *unit* substance was responsible for the graphic structure. This is probably not determinable, in most cases. Frequently, however, some supporting evidence serves as an aid in the solution of the problem. Thus, evidence



FIG. 3.—Graphic structures. Sphalerite earlier, Jamesonite later. Jamesonite replacing sphalerite. $\times 300$.

Dark gray streaks, patches, and masses are sphalerite; the white areas are jamesonite. There are illustrated here: (a) graphic structure, (b) replacement structure, (c) inclusions (remnants of sphalerite in jamesonite), and (d) jagged and penetrating structures.

It is impossible to determine whether the graphic structure has resulted from the replacement of some other component of the sphalerite that was originally intergrown with it, or whether the graphic structure is due to the irregular replacement of the sphalerite itself. There are replacement remnants of sphalerite in the jamesonite that aid in the judgment of sequence (compare Fig. 4).

for enreachment, corrosion, or replacement may be so closely connected with the graphic intergrowth that less difficulty is experienced in determining its origin when such associated structures are present. The nature of the boundaries does not

usually help much, since they may be smooth in any case; nor is the mere existence of graphic structures a criterion for either simultaneous deposition or diversity in age. Additional supporting evidence is always needed. These structures do not, therefore, serve as criteria for one origin or another nor for sequence in mineralization but must themselves be interpreted

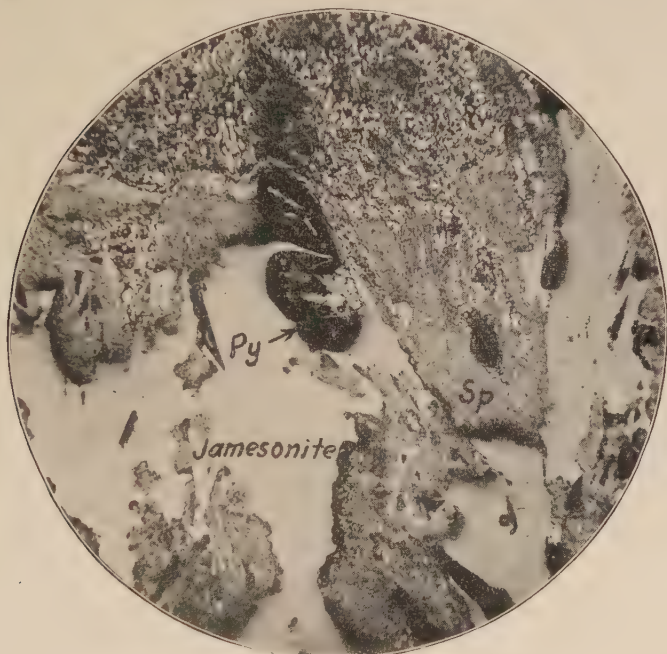


FIG. 4.—The same polished plate shown in Fig. 3, but at a lower magnification.
×40.

Jamesonite (white), sphalerite (gray), and pyrite (black and white areas).
Illustrating: (a) graphic structure, (b) jagged and penetrating structures, (c) encroachment and embayment, (d) replacement remnants, and two distinct mineralization epochs.
Epoch I: Pyrite-sphalerite mineralization.
Epoch II: Jamesonite mineralization.
Jamesonite is replacing both pyrite and sphalerite. It represents a sharp, distinct change in mineral composition, which may be interpreted here as a change in mineralization epochs, because the structural evidence and boundary relations show jamesonite to be later than and encroaching upon the earlier sphalerite and pyrite.

on the evidence presented by existing structures connected with them. Figures 3 and 4 are illustrative of some of the features mentioned. Jamesonite and sphalerite occur in graphic structure, but on the basis of the structure alone it would be impossible to say whether the two minerals were deposited simultaneously or whether one replaced the other. Associated structures of replacement type, however, determine the sequence;

jamesonite shows replacement relations to both sphalerite and pyrite; and since, in other parts of the polished surface not illustrated, sphalerite encroaches slightly on pyrite, the sequence may be determined to be (1) pyrite, (2) sphalerite, (3) jamesonite. This also indicates the graphic structure to be a replacement product, and there is likewise suggested the possibility of two mineralization epochs. The pyrite and sphalerite belong to the earlier epoch, whereas the jamesonite belongs to Epoch II.

2. *Concentric Structures*.—Although not common in metallic ore minerals, concentric structures sometimes occur. They may result from (a) simple sequential deposition or (b) rhythmic precipitation. They usually indicate contemporaneity, although the possibility of an inherited concentric structure due to the replacement of some former mineral, which originally had that structure and which was preserved during the replacement, must be kept in mind. Concentric structures, therefore, are not criteria for diversity in age, but they may be connected sometimes with replacement processes as structural remnants from an earlier mineralization epoch.

3. *Banded Structures*.—Symmetrical banding in ore minerals has been commonly regarded as an evidence of continuous deposition during a single mineralization epoch. Banding is commonly connected with deposition in veins, and the normal sequence of mineralization is believed to have been from the walls of the vein inward toward the center. That is, the ore minerals adjoining the walls are supposed to be earlier than those nearer the center of the vein.

Both concentric and banded structures may be explained as rhythmic precipitation during the *gel* stage of ore deposition; hence, they may be regarded as essentially contemporaneous in origin but with a continuity which may be interpreted in terms of sequence. It is possible, therefore, that even in banded veins the ore minerals are contemporaneous in origin. Such slight age differences as may exist are difficult to interpret, but the *earlier* minerals may really be precipitated at or near the center of the vein and later ones out near the walls, thus reversing the usual conception of sequence in vein structures of this kind.

4. *Cores*.—Cores of one ore mineral, surrounded by envelopes of a different mineral or by envelopes whose composition differs from that of the core, are regarded as excellent criteria for

mineral sequence (the core being the earlier mineral); in many cases, such structures are also used as absolute evidence of replacement and as proof of two different epochs of mineralization. It is generally true that if one ore mineral is enveloped by another that has a different composition, especially if the contact between the core and the surrounding envelope is irregular, the core is earlier in time of deposition, the envelope later and a product of replacement processes. Hence, such structures are criteria for sequence, replacement, and two mineralization epochs. But these structures may originate in other ways; therefore, caution must be exercised in their interpretation. They may be due to (a) zonal growth (progressive change in composition during crystallization); (b) abrupt change in composition, probably occurring by reason of the gradual concentration of certain impurities in the mineralizing solution until their concentration is such as to cause them to be coprecipitated with the ore mineral; or (c) oxidation.

Light-brown sphalerite with black borders (envelopes) of the same substance, rich in iron and manganese, is an example of abrupt change in composition; here the *core* and the *envelope* are both sphalerite, and they both belong to the same mineralization stage. Pyrite crystals are at times surrounded with black borders resembling envelopes of supergene chalcocite; in ores carrying a little copper and silver, such structures are deceptive, since, frequently, they are merely black oxidation products of the pyrite itself and are not products of downward sulphide enrichment at all.

5. *Inclusions*.—Inclusion of one ore mineral in another may have likewise more than one origin. When the inclusions are minute, with smooth margins and round or oval forms, they may usually be regarded as contemporaneous with the mineral which acts as host; they were originally in solution in the host mineral and have precipitated in the host either during or subsequent to the crystallization of it. An example of this condition is offered in the minute round specks and grains of chalcopyrite which are frequently distributed in sphalerite. If the inclusions are oriented along structural directions in the host so that a symmetrical pattern results, the included mineral may be likewise contemporaneous with the host; but caution is needed in dealing with a structure of this character, since replacement processes may produce the same effect. Provided, however, that the

included mineral has an erratic distribution and very ragged, embayed boundaries, it is legitimate to deduce that such inclusions are replaced remnants of an earlier ore mineral and that sequence and replacement are represented.

Replacement remnants occurring as inclusions in the replacing mineral are illustrated in Figs. 4 and 5. Pyrite, in Fig. 4, is



FIG. 5.—Covellite, bornite and chalcocite. $\times 40$.

Illustrating: (a) jagged and penetrating structures, (b) inclusions (replacement remnants), and (c) two mineralization epochs.

Covellite (Cv) very dark gray. Bornite (B), light gray patches in the chalcocite. Chalcocite (Cc), white.

Chalcocite corrodes and replaces bornite, which is here a remnant of the earlier mineralization and is judged to belong to the first mineralization epoch. The relation between the dark-blue covellite needles and the chalcocite is not so clear. Each penetrates the other, and the covellite carries inclusions of chalcocite. The chalcocite in places has corroded the covellite, and this serves as supporting evidence for the sequence: bornite—covellite—chalcocite.

included in jamesonite, which is the replacing mineral. In Fig. 5, bornite remnants are distributed in a heterogeneous manner in chalcocite; the bornite boundaries are extremely irregular, and embayments are prominent. In such cases as these, there is little doubt as to the nature of the process and the paragenesis.

6. *Corrosion Structures, Cross-cutting Structures, and Pseudomorphs.*—These structures furnish absolute evidence for diversity in age and, frequently, for more than one mineralization epoch. If one mineral exhibits ragged, embayed, and highly crenulated margins against another, it is safe to assume that the mineral possessing such boundaries has been attacked and partially replaced by the other mineral; moreover, the attacking or replac-

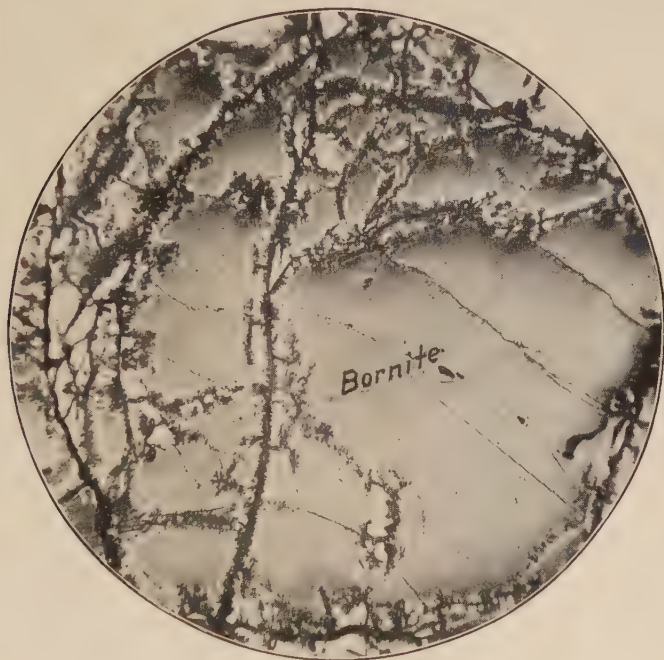


FIG. 6.—Bornite with veinlets of chalcocite and chrysocolla. $\times 40$.

Illustrating: two mineralization epochs, determined by the later, cross-cutting structures traversing the earlier bornite. Note that the chalcocite in the veinlets is associated with, and is itself cut by, chrysocolla. The bornite is of hypogene origin and belongs to the first mineralization epoch. The chalcocite and chrysocolla are supergene in origin, belonging to a much later, second mineralization epoch.

ing mineral not uncommonly corrodes or replaces more than one of the earlier minerals, so that no difficulty is experienced in establishing an accurate sequence. When more or less intense deformation has operated on the ore minerals of the initial mineralization epoch, so that fracturing and brecciation have affected the ore minerals and this has been followed by later additional mineralization, cross-cutting structures result, furnishing absolute and perfectly determinable criteria for the

interpretation of the processes involved. In such cases, usually no difficulty is experienced in establishing (a) sequence for the minerals of the first mineralization epoch; (b) a deformation unconformity; (c) sequence for the minerals of the second mineralization epoch; and (d) replacement.

Pseudomorphs of one mineral after another, or of an aggregate of minerals collectively pseudomorphous after another mineral, are equally good criteria for judging sequence and replacement. Replacement structures are illustrated in Figs. 3, 4, and 5. Cross-cutting structures are shown in Figs. 6 and 7. In Fig. 6,

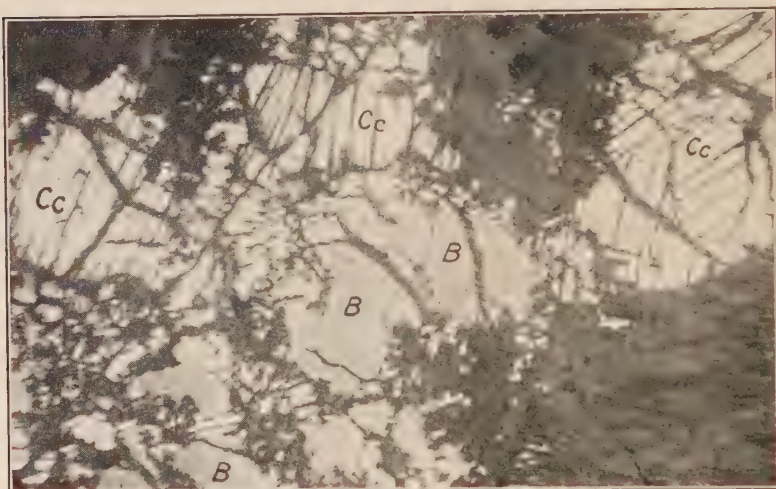


FIG. 7.—Reticulate structure. Bornite (B) replaced by chalcocite (Cc). $\times 85$.

Both bornite and chalcocite are in turn cut by veinlets of chrysocolla. Where the chrysocolla cuts the chalcocite it follows structural weaknesses producing a sort of reticulate structure. Where the bornite is cut by veinlets, chalcocite forms the outer margins of the veins in contact with the bornite, whereas the centers of the veins consist of chrysocolla. There are illustrated here: (a) two mineralization epochs, (b) cross-cutting and reticulate structures, and (c) replacement boundaries.

bornite is fractured and veined with chalcocite which has encroached on the bornite and replaced it beyond the initial fracture limits. Chrysocolla is associated with the chalcocite, occupying the centers of the veinlets; it exhibits structures suggestive of precipitation from a gel, and it seems probable that the chalcocite and the chrysocolla are closely connected in origin and in time of deposition. In Fig. 7, the chalcocite, which is replacing bornite, exhibits a *reticulate structure*, emphasized by the associated chrysocolla. It is possible that this structure is inherited from the bornite, but there is no proof of it.

7. *Incongruity in Mineral Association.*—The presence of one or more minerals whose composition and behavior indicate that they may have formed under quite different conditions of pressure and temperature from the other minerals in the ore is also suggestive of two different and distinct epochs of mineralization, even though no other evidence of the two epochs can be found. Figures 6 and 7 illustrate incongruity, since bornite and chrysocolla have origins prohibitive of contemporaneous deposition. In both cases illustrated, however, the additional evidence of cross-cutting structures is offered. The association of minerals formed under high temperatures and high pressures, with minerals originating in the zones of low temperatures and moderate pressures, is suggestive of a more complex mineralization history than would appear at first glance. Such anomalous association, in the absence of other evidence, must be interpreted with much caution; a contemporaneous origin must not be inferred invariably from cases of this kind, since it is possible that two distinct mineralization epochs may be represented notwithstanding the absence of other and confirmatory structures. All of the foregoing criteria may be conveniently assembled as follows:

I. Evidence for Contemporaneous Deposition

1. *Simultaneous Precipitation:*

- a. Aggregates of allotriomorphic grains, especially if the grains are approximately all the same size.
- b. Concentric and banded structures which may be explained on the basis of rhythmic precipitation from a gel.

2. *Continuity in Deposition:*

- a. Smooth contacts, either straight or curving, between adjacent grains.
- b. Interstitial distribution of one or more of the ore components in such a manner as to fill spaces between the other, and usually larger, grains.
- c. Possibly some graphic intergrowths.
- d. Inclusions of one mineral in another, provided (1) the inclusions are minute, round or oval globules, sparsely and irregularly distributed; (2) the association is not incongruous; (3) the inclusions are symmetrically oriented and are relatively small in amount.
- e. Concentric arrangements and alternating bands of two or more minerals, on such a scale that some continuity in sequence may be determined.
- f. Zonal growths, provided the different zones are of the same mineral; the composition changes slightly from center to edge.

II. Evidence for Diversity in Age

1. *Some Graphic Structures:*

It should be remembered, however, that frequently supporting evidence is necessary for the interpretation of sequence in these cases.

2. *Cores:*

Especially when the boundaries between the core (replacement remnant) and its surrounding envelope are very irregular, and provided some incongruity in composition or association exists. Caution is needed in the interpretation of these structures, because they may have other origins.

3. *Inclusion of One Mineral in Another—Provided:*

a. Association incongruity obtains.

b. The included mineral exhibits extremely irregular, embayed, and highly crenulated margins against the host. Caution should be exercised here, likewise, since some minerals of strong crystallizing force may control their boundaries, thus exhibiting sharp, straight crystal edges.

4. *Corrosion Structures:*

The boundaries between the mineral attacked and the mineral attacking are usually irregular, crenulated, and embayed. Such marginal relations commonly indicate the operation of replacement processes.

5. *Cross-cutting Structures:*

Veinlets of one mineral in another. Not only diversity in age is indicated, but also more than one mineralization epoch and a history of deformation subsequent to the initial mineralization time, as well.

6. *Pseudomorphs:*

Either unit pseudomorphs of one mineral after another, or aggregates of minerals pseudomorphous after another. These structures serve as positive criteria for replacement.

7. *Splintery, Jagged, and Penetrating Structures.*

8. *Incongruity in Association.*

Thus a sequence may be simple and confined to one mineralization stage, so that the minerals are all essentially contemporaneous in origin but with continuity in deposition; or a sequence may be complex, involving either a series of progressive replacements with consistent changes in composition, such as the changes—chalcopyrite—bornite—covellite—chalcocite; or exhibiting two distinct epochs, separated by either (a) at totally different series of products of different type, or (b) deformation unconformity, indicated by veinlets cutting all members of the earlier mineralization epoch and containing a different assemblage of minerals.

CHAPTER VIII

THE MICROSCOPIC CRITERIA OF REPLACEMENT IN THE OPAQUE ORE MINERALS

BY W. H. NEWHOUSE

Introduction.—The study by the reflecting microscope of opaque minerals in polished sections has greatly increased in the last decade. Various workers have recorded data necessary for mineral determination, and these data have been made available for general use. Each worker in the polished-section field has, however, very largely developed his own criteria for the interpretation of the structures observed. In large part, the criteria used have been developed by *a priori* reasoning, as to what should happen under assumed conditions of mineral deposition. The literature consequently contains many different interpretations of common structures in the ore minerals. The writer believes that the only sound solution to most of these problems of interpretation is to be found in the data obtained by experimentation and from examples which have been very carefully selected from nature. With this in mind, a number of artificial replacements have been made in the laboratory, and some carefully selected examples of replacement from nature have been studied, to obtain the data on the structures formed by replacement. The material examined falls into three general classes: (1) artificial replacements; (2) replacement of sulphides and oxides by oxidation products; and (3) partial pseudomorphs of sulphide and oxide crystals. These three kinds of material all display the same general types of replacement structures. There is a tendency, at times, for the host to form a boundary which is concave outward in replacement by oxidation products.

The oxidation products also form, in general, sharper angles along the boundary line between the replaced and the replacing mineral and develop the cleavage of the host perhaps more than the others. The rule by no means always holds, for some pyrite which is being replaced by limonitic products shows a quite undulating or sinuous boundary between the two.

Replacement¹ may be defined as

The process of practically simultaneous capillary solution and deposition by which a new mineral of partly or wholly differing chemical composition may grow in the body of an old mineral or mineral aggregate.

The solutions which cause replacement may be either liquid or gaseous in nature and of high or low temperature.

The occasional formation of solution cavities, with later filling by another mineral, might give structures very much like those of replacement. Such cavities are probably of no quantitative importance in the deeper zones and will not be considered in this paper.

The material on which the study was made will be described first, after which the criteria of replacement will be given.

Artificial Replacements.—The artificial replacement of chalcopyrite by bornite and of chalcopyrite and bornite by chalcocite and covellite has given some very interesting results. These replacements were effected by immersing the polished and examined sections in a copper-sulphate solution and, in some experiments, passing sulphur dioxide through the solution. Solutions of different strength were used on different lots of specimens. Some of these were held at room temperature, while others were placed in an oven and held at temperatures varying with different lots, from room temperature to about 80°C. Some of the lots were held in solution only a few days, while others were left for about 6 months.

Hematite was artificially replaced by magnetite in several different types of specimens. Magnetite was, in turn, replaced by hematite and also by *brownish magnetite* (?)²

These replacements were made by using a blow torch or gas furnace. Hematite was partly reduced to magnetite by the reducing flame, and magnetite was, in part, oxidized to hematite or to *brown magnetite* (?) by using the oxidizing flame. The *brown magnetite* appears to form at a lower temperature than the hematite, while both are usually related to the border or to cracks and openings, of the specimen in which they form. In these artificial replacements, the prospective host-mineral specimens were selected so that different grain or crystal sizes

¹ LINDGREN, W., "Mineral Deposits," p. 103, 1927.

² NEWHOUSE, W. H., and W. H. CALLAHAN, "Two Kinds of Magnetite?", *Econ. Geol.*, Vol. XXII, pp. 629-632, 1927.

were represented. In some, a large proportion of the specimen was composed of inert minerals; in others, practically none.

Replacement by Oxidation Products.—Pyrite, pyrrhotite, chalcopyrite, and magnetite aggregates of crystals partly replaced by limonitic minerals, and aggregates of galena crystals partly replaced by cerussite and anglesite, were examined. Some euhedral crystals of pyrite replaced by limonite, and euhedral crystals of galena replaced by anglesite and cerussite, were studied.

Partial Replacement in Pseudomorphs.—It is realized that some complications may ensue in using pseudomorphs as a positive means of knowing that one mineral is later than and replaces another. For instance, hematite might form a small crystal, which was, later, partly replaced and completely surrounded by a euhedral magnetite crystal. Later, partial replacement of this magnetite crystal by hematite would give rise to two generations of hematite associated with the magnetite. With care, however, and especially by studying a number of different mineralogical combinations in pseudomorphs, this source of possible error can be largely eliminated. The kinds of partial pseudomorphs used in the study are listed in the following paragraph:

- Euhedral magnetite crystals partly replaced by hematite
- Euhedral pyrite crystals partly replaced by chalcocite
- Euhedral pyrite crystals partly replaced by limonite
- Euhedral tetrahedrite crystals partly replaced by bournonite
- Euhedral enargite crystals partly replaced by chalcocite
- Euhedral bornite crystals partly replaced by chalcocite
- Euhedral bornite crystals partly replaced by chalcopyrite
- Euhedral galena crystals partly replaced by anglesite and cerussite

CRITERIA OF REPLACEMENT

The criteria developed on the following pages are based on the spatial relations shown by replaced to replacing mineral in the examples studied. It has been the more common custom of American workers on polished sections to consider minerals as the units for discussion. It is believed by the writer that a more fundamental treatment would usually consider crystals as the units. This idea has been adhered to as closely as possible in the study of data and, also, in the discussion of results.

Many other criteria for replacement can be obtained from the larger relations, particularly those relations observed in the

field. Such may often be more convincing and of more value than these microscopical criteria, but they do not enter into the province of this paper and will not be discussed.

It cannot be too strongly emphasized that no one microscopical criterion given is usually sufficient to prove replacement. A single microscopic field will usually not furnish enough data to convince one that replacement has occurred. Hence, a photograph of a selected portion of a polished section will seldom demonstrate it. On account, doubtless, of this fact, many of the published photographs which are supposed to show replacement fail to convince one. In this paper, sketches of general cases have been used to illustrate the criteria, because much more information can be put into such a sketch than can readily be obtained in a drawing or photograph of an actual microscopical field. The scale of magnification adopted might be greatly changed without materially affecting the results.

Although the actual structures observed were used in building up the criteria, reasoning must enter to explain and classify the results and to show how these will differ from other structures formed by unmixing, by solution of two minerals to form one,¹ or by contemporaneous deposition. Mistakes on this score probably have been made, but that is inevitable until these other fields have been experimentally explored and the findings described. In general, great irregularity of form, and in amount and place of development, of a mineral may argue against unmixing as a means of a structure's formation. Exceptions to this rule may be expected, however, especially those changes due to original differences in composition of the mineral which suffered breakdown.

The criteria will now be discussed.

Veinlets.—A veinlet may have straight parallel walls, or irregular matched or unmatched walls. Its relations to the crystals which enclose it are of the first importance. If the veinlet is straight and with approximately parallel walls, the first question should be, Does it follow crystallographic directions in one crystal, or does it extend indiscriminately across many crystals? If a veinlet is irregular, the first question should be, Does it *crosscut* the host crystals, or does it go between them? For purposes of discussion, the veinlets will be divided into two

¹ WANDKE, A., "Molecular Migration and Mineral Transformation," *Econ. Geol.*, Vol. XXI, pp. 167-168, 1926.

classes, those that crosscut the host crystals, and those that go between them.

Veinlets Which Crosscut or Transect the Host Crystals.—Residual fragments left by replacement may be attenuated and somewhat like veins in appearance; so, unless the masses are very long and narrow and cut through a number of crystals, the evidence for replacement based on this feature is not convincing. Where several veins with unmatched walls crosscut or transect many *diversely oriented host crystals*, it may be considered strong evidence of replacement. This is especially true where the

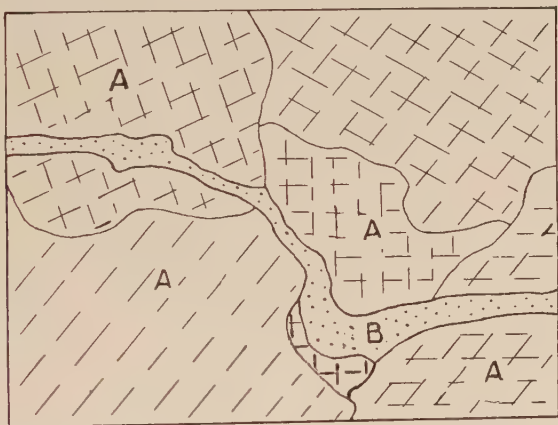


FIG. 1.—Diversely oriented crystals of a host mineral (A) with a replacement vein of a later mineral (B). The parallel lines of (A) are intended to represent merely some crystallographic direction like twinning or cleavage. ($\times 10$.)

cleavage of the host is occasionally developed along the vein boundary.

When veins composed of one mineral are related to crystallographic directions in the host and do not extend continuously into other crystals beyond the one host crystal, this criterion will not usually decide whether replacement or exsolution has occurred. Examples are the familiar small veinlike masses and scattered blebs of chalcopyrite and pyrrhotite in sphalerite and the blades of cubanite in chalcopyrite.

The interpretation of this type of structure is one of the most difficult problems facing the polished-section worker of today. Schwartz¹ has definitely shown that cubanite may form such

¹ SCHWARTZ, G. M., "Intergrowths of Chalcopyrite and Cubanite," *Econ. Geol.*, Vol. XXII, pp. 44-61, 1927.

intergrowths with chalcopyrite by exsolution on lowering the temperature of a solid solution of the two.

On the other hand, the writer has found good evidence that the small scattered blebs and veinlets of chalcopyrite occurring along crystallographic directions of sphalerite have, in some cases, been formed by replacement. In ore from Clear Creek, Colorado, some quartz-chalcopyrite veins occur along fractures in the sphalerite. Diversely oriented sphalerite crystals have been fractured with quartz and chalcopyrite later introduced along the fractures. Many small chalcopyrite inclusions developed partly

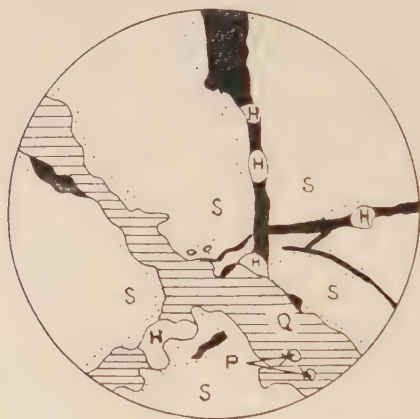


FIG. 2.—Camera lucida drawing of veins of chalcopyrite (black mineral) and quartz (*Q*) cutting sphalerite (*S*), with chalcopyrite blebs (dots) in a narrow border of sphalerite next to the vein. Hole (*H*), Pyrite (*P*), Clear Creek, Colorado. ($\times 430$.)

along crystallographic lines are found in a narrow border of the sphalerite adjacent to the quartz-chalcopyrite veins.¹

Very similar structures have been observed in ore from the Sheldon Mine, from the Poland Tunnel, and from the Wild Flower Mine all in the Jerome-Bradshaw Quadrangle, Arizona. Of course, these few examples do not prove that all examples of these blebs in sphalerite are of replacement origin.

Some evidence is at hand which tends to prove that some of these structures may be formed in two ways, for "chalcopyrite gratings in bornite . . . have been produced artificially by

¹ NEWHOUSE, W. H., "An Examination as to the Intergrowth of Certain Minerals," *Econ. Geol.*, Vol. XXI, pp. 68-69, 1926.

Lombard and Merwin¹ by the action of heated sulfur vapor on bornite and by the unmixing of a bornite solid solution containing an excess of iron over that necessary to form pure bornite."

They have also been produced by immersing bornite in a cupric-sulphate solution.²

Still another possibility remains for certain structures showing a relation to the cleavage of one of the minerals—that of contemporaneous deposition to form graphic intergrowths.

The origin of these graphic structures in the sulphide ores is still a subject for debate and must await evidence for a solution. Locally, they may look very much like certain of the metallic eutectics obtained by the metallurgists. This, of course, does not prove that they are eutectics. An analogy may be seen in the grating structure of chalcopyrite in bornite, which not only looks like an unmixed structure but has actually been produced as one, *yet it clearly may also form by replacement*, as has been mentioned. Until something is known as to how the graphic structure has formed in ores, its value is negligible as proof of anything.

In summary, veinlike masses related to cleavage directions in the host may be several origins. Such a structure must be used in combination with other features in order to prove replacement.

Veinlets between Host Crystals.—Replacing solutions often appear to find ingress to the ore most readily between crystals. Where each host crystal has been surrounded by a guest mineral, so far as this structure alone is concerned, a number of alternative processes other than replacement might be responsible for the relations. The feature in itself would appear to have little value as a criterion, but taken in connection with several other things it might carry weight.

Cusps, or Incipient Veinlets.—Cusps may be regarded, in some instances, as incipient veinlets. Commonly, they project between two crystals. When a cusp has been formed by replacement, and one of the two earlier crystals has acted as an inert substance, a characteristic pattern frequently results.

¹ Quoted by SHORT, M. N., and I. A. ETTLINGER, "Ore Deposition at the Magma Mine, Superior, Arizona," *Trans. Am. Inst. Mining Met. Eng.*, Vol. LXXIV, p. 205, 1926.

² ZIES, E. G., E. T. ALLEN, and H. E. MERWIN, "Some Reactions Involved in Secondary Copper Sulphide Enrichment," *Econ. Geol.*, Vol. XI, pp. 446-479, 1916.

In the sketch, 1 is an inert mineral, like quartz, 2 is a mineral which either crystallized in part earlier than 3 or was partly replaced by 3. A careful examination of the angles made between 1 and 2 by cusps of 3 will often show that the greater portion of these are acute angles. Evidently this may be due either to the replacement taking place more rapidly along boundaries between crystals than elsewhere or to an overlapping of mineral deposition. Where irregularity in spacing and development rules, and these cusps follow cleavage directions of the

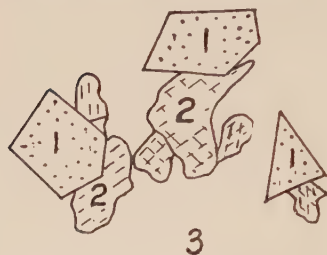


FIG. 3.—Cusps forming along crystal boundaries of the host. (1) is an inert mineral; (2) is partly replaced by (3) the cusps of which prefer the cleavage directions of (2). ($\times 20$.)

host, the evidence for replacement is good.

Advance Islands of the Guest in the Host Mineral.—The fabric formed by advance islands of the guest in the host depends on the relative sizes of crystals of the two minerals. When the

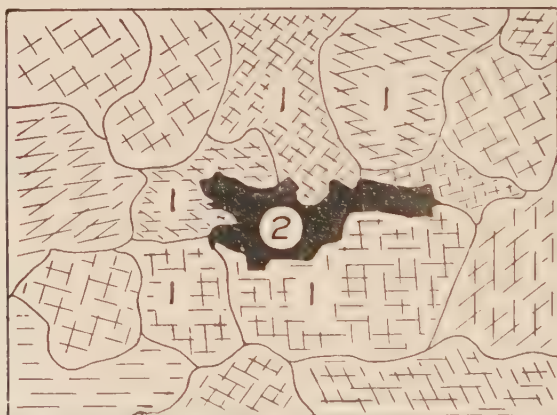


FIG. 4.—Advance island of one mineral (2) in another (1). (2) has replaced (1) to some degree at its boundaries along crystallographic, probably cleavage, direction. Lines in (1) indicate cleavage directions. ($\times 10$.)

host crystals are large in relation to the guest crystals, the replacement is likely to show a relation to the boundaries of the former. Inspection of a number of such advance islands will sometimes show that they have their shape by virtue of the

general crystal boundaries and the vectorial (replaceable) directions in the host mineral or minerals.

The value of this criterion is almost entirely dependent on the guest mineral's developing cleavage directions of the host crystals. The mere existence of an irregular island of one mineral in another is of no significance whatever. Such islands, both large and small, with smooth and sinuous or angular boundary, singly or in groups, are common in replacement and occur in either the host or the guest mineral. They may probably be formed in other ways, such as by contemporaneous deposition as well as by replacement.

A euhedral guest crystal in a host sulphide is a special and not very common occurrence in the sulphide ores. Occasionally, the sulphides with a strong force of crystallization, such as pyrite or arsenopyrite, may show crystal faces along replacement veinlets in other sulphides, but the writer knows of no occurrence of galena, sphalerite, tetrahedrite, or chalcopyrite's forming such faces when the evidence was clear that they had been formed by replacement of other sulphides.

Preferential Replacement of One Mineral in a Mixture by a Later One.—Replacement may proceed as a wave which sweeps everything before it, or it may search through the ore and replace selectively. When it sweeps through as an all-destroying wave, the evidence for it can be found, usually, only on the frontiers or along the border line. Along the border line, even in this case, it often shows a preference for certain minerals, some of which may be partially, others wholly, removed.

In the other type, where only one or two members of an ore mixture are replaced, a general dividing boundary between replaced and replacing minerals may not exist. Instead, the guest is dispersed throughout the host. Neither of these two extremes in manner of replacement is the usual thing. One mineral may be attacked before others, but some remnants of it usually remain even after the more resistant minerals have been largely replaced.

In the beginning of a replacement in which one mineral is replaced more readily than others, tongues of the replacing mineral sometimes encroach on the host, particularly along crystal boundaries, cleavage directions, or incipient fractures; and cusps of the replacing mineral may result. Within the edge of a wave, corroded remnants which may occasionally

outline a ghost crystal sometimes remain in the replacing one, while beyond are unreplaced crystals.

Conclusive proof of replacement is seldom obtained where selective action is the sole feature observed. The different structures described elsewhere may, however, when added to this one, form a definite proof.

Replacement along Cleavage or Other Crystallographic Directions in the Host Mineral.—Veinlets along cleavage directions in the host have been treated in the previous discussion. It is intended to include here general boundaries, or crystals in a matrix showing frequent correspondence of boundary to cleavage of the host.

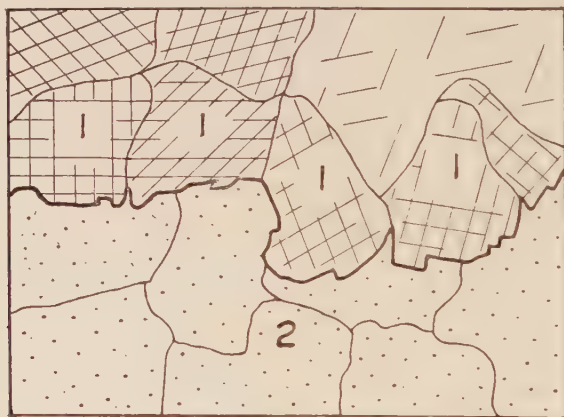


FIG. 5.—Mineral (2) replacing (1) along its cleavage directions. Size of reentrants is exaggerated over that commonly found in such a hypogene mineral replacement as galena replacing sphalerite. ($\times 10$.)

When used with caution, this feature constitutes one of the most valuable criteria. Where large areas of the two minerals have a common boundary which shows straight edges and angles parallel to the cleavage of the host, good evidence is at hand for replacement. Straight edges and angles may, of course, be due to natural crystal faces; but where a reentrant angle occurs on a crystal and examination proves this crystal is untwinned and without parallel growths, the possibility of their being natural crystal faces is eliminated. It should be remembered that a crystal may have a reentrant angle due to its being deposited on a euhedral crystal such as arsenopyrite. In order

to be used as a proof of replacement, the sides of the reentrant angle should show parallelism with the cleavage of the host.

Cleavage may be demonstrated by pits, as in galena and pentlandite or, occasionally, sphalerite, by chemical etching, or by the relation to twinning. Twinning may be revealed by chemical etching or, in some minerals, by the use of reflected polarized light. By proper manipulation in polishing, some minerals, such as chalcopyrite or sphalerite, may be eroded so as to make the twins stand in relief.

Residuals or Remnants Left by Replacement.—These constitute an important criterion of replacement. A single residual



FIG. 6.—Residual masses of mineral (1) in replacing mineral (2). The masses of (1) all have the same orientation, are smaller in general near the outside, are very irregular in outline and in arrangement. ($\times 20$.)

The boundaries of (1) frequently correspond to its cleavage directions. These cleavage directions are not otherwise indicated in the diagram, and they would have to be determined on the mineral in actual microscopic work.

mass left by replacement will usually have little diagnostic value; but, in a number of such residuals are examined as to their relative sizes and their relations to each other and to the replacing mineral, definite conclusions may often be drawn. Advance islands of a guest mineral may be confused with residual masses or with area formed by contemporaneous deposition, but when a number of such islands is examined, characteristic features may often be found. A large residual mass may be broken up into smaller ones having a common orientation. This may be significant if the dissected grain, as outlined by its

residuals, still retains the general size and shape common to it in the unreplaced host. The masses in such a dissected grain frequently show gradation in size, the outermost ones of the group being smaller, with larger masses in the central part. If cleavage directions are developed along the boundary of the host, the criterion gains much in value. If a skeleton crystal of one mineral had another mineral deposited around it, the above conditions might, however, be approximated. The skeleton crystals of magnetite, chalcopyrite, pyrrhotite, and other sulphides which the writer has seen have been characterized by a general regularity of development. Replacement, on the other hand, is usually irregular in its results, which should aid in distinguishing such structures.

APPLICATION OF THE CRITERIA

In general, no one example of a single criterion can be regarded as having weight enough to demonstrate replacement. There should be a convergence of evidence based on several structures illustrating the criteria discussed, before an example can be regarded as proved. For most of the structures described on previous pages, another explanation, or sometimes several others, can be given besides that of replacement. Where several criteria are obtained, however, the same alternative explanation may not fit them all. Sometimes several of the structures may be found in a small space on one section; but, to judge from the known examples studied, they frequently will not, for many fields in these examples which were studied show no evidence of replacement. Lack of evidence of replacement in one or several adjacent fields or in several sections cannot be considered proof of contemporaneity, any more than can lack of proof of contemporaneity be considered proof of replacement.

The judgment of the individual will probably play a large part in the interpretation of replacement structures in ores for some time to come. To make the rules completely foolproof would seem to be impossible with the present development of the science.

Extent of Replacement in Hypogene-sulphide Ores.—Study indicates that replacement of one sulphide by a later one plays a considerable part in massive sulphide ore bodies. In fact,

successive partial replacement of earlier sulphides by later ones seems to be the rule. If the criteria developed on the foregoing pages are uncritically used, the polished-section student may easily be led into the belief that, quantitatively, this relation is larger than may really be true. It is also true that, as replacement proceeds, it destroys its own footprints, and so it is only on its frontier that evidence is found.

This may lead to the opposite extreme, and the amount of replacement be underestimated.



FIG. 7.—Camera lucida drawing of an "intimate intergrowth" of pyrite (black) and limonite (white). The limonite is replacing the pyrite, in a partial pseudomorph of limonite after a pyrite cube. ($\times 45$.)

Intimate or Intricate Intergrowths as Proof of Contemporaneous Deposition.—It may be regarded as certain that overlapping of mineral deposition takes place. In fact, the banded veins where two or more minerals are found in the same band indicates that minerals are frequently deposited with overlapping or contemporaneous periods of deposition. Although proof that one mineral has partly replaced another is frequently found in sections, the proof of contemporaneous deposition is, unfortunately, often very hard to obtain.

Some writers¹ have used the presence of intimate or intricate intergrowths between minerals as proof of their contemporaneous deposition. Often such intergrowths are admitted to grade out in the same microscopic field or in the same section into replacement structures. The illustrations commonly show islands, or masses of the minerals in each other, with very irregular boundaries and no veinlets showing in the field.

These may have been formed by contemporaneous deposition; but such intergrowths may also be formed by replacement, for in the polished sections examined in the present study many highly irregular areas of guest in host, and of host in guest, were found, with none of the diagnostic features of replacement in the field.

Mutual Boundaries as Proof of Contemporaneous Deposition.—The mutual-boundary pattern has also been used as a proof of contemporaneous deposition.²

Short describes the *mutual-boundary pattern* as follows: "If the pattern made by two adjacent minerals is smooth and regular or forms regular curves with no decided projections of one mineral into another it is termed the mutual boundary pattern."

The assumption back of this must be that replacement does not "form regular curves with no decided projections of one mineral into another."

The writer found in the study previously described that replacement may and does frequently form smooth, regular curves with no decided projections of either host mineral or guest mineral into the other. Since this is true, the mutual-boundary relation can have no particular significance in interpretation of mineral relations.

A section cut perpendicular to the present one and through A-A would doubtless show rounded areas of chalcocite in bornite,

¹ BASTIN, E. S., "Silver Enrichment in San Juan Mountains, Colo.," *U. S. Geol. Sur. Bull.*, 735, p. 82, 1922. "Silver Ores of Aspen, Colo.," *Bull.* 750, *idem*, p. 46, 1923-1924. "Silver Ores of South Lorraine and Cobalt, Ontario," *Econ. Geol.*, Vol. XX, p. 16, 1925.

EMMONS, W. H., and F. B. LANEY, "Geology and Ore Deposits of the Ducktown Mining District, Tenn.," *U. S. Geol. Sur., Prof. Paper* 139, p. 47, 1926.

² LOCKE, A., D. A. HALL, and M. N. SHORT, "Role of Secondary Enrichment in Genesis of Butte Chalcocite," *Trans., Am. Inst. Mining Eng.*, Vol. LXX, p. 955, 1924.

SHORT, M. N., and I. A. ETTLINGER, "Ore Deposition and Enrichment at the Magma Mine, Superior, Arizona," *Trans., idem*, 74, p. 24, 1926.

with smooth and regular curves. Some of these areas might well show no connection whatever to the vein. Many references may be found in the literature where small isolated areas of one

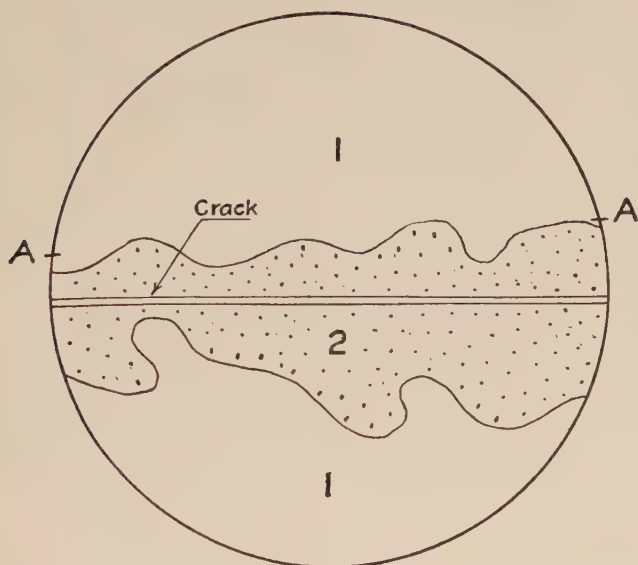


FIG. 8.—Chalcocite (2) replacement vein along crack in bornite (1). Formed artificially by placing bornite in copper sulphate solution at room temperature for several weeks. The boundary is a replacement one and shows no projections nor "fuziness" even at the high magnification used. This proves that replacement can give boundaries having smooth regular curves, in other words that it may form "mutual boundaries." ($\times 1,400$.)

mineral in another has been used as proof of the contemporaneous deposition of the two. The necessity of thinking in terms of three dimensions rather than just two, in the interpretation of polished sections, is apparent.

CHAPTER IX

THE TEXTURAL RELATIONSHIPS OF THE OPAQUE MANGANESE MINERALS

BY G. A. THIEL

Introduction.—The textural relations of the opaque manganese minerals must be thoroughly investigated before any problems dealing with metallurgical processes or chemical and mineralogical constituents of manganese ores can be interpreted intelligently. From a study of the microstructure of such ores, it is evident that many alterations and replacements can be expected. As a group, the minerals show no uniform order of deposition. There seems to be no systematic change from manganous to manganic forms, nor is there a definite order from the more hydrous to the less hydrous, or *vice versa*. The widespread replacement of other manganese minerals by pyrolusite, however, suggests a tendency toward progressively higher oxidation and, in many cases, dehydration following the initial precipitation.

The following alterations and replacements represent some of the common relations observed in ores from widely separated districts and from a variety of geologic settings.

Pyrolusite (MnO_2).—Pyrolusite is, perhaps, always secondary except where it occurs as a primary constituent of sedimentary beds. It is frequently found as reniform coatings associated with other manganese minerals. It is commonly columnar and also granular massive. A high percentage is pseudomorphic after radiating needles of manganite. Polished surfaces of ore specimens from the southern Appalachian manganese deposits show many remnants of manganite grains that have not been entirely replaced by pyrolusite. In other districts, it is pisolitic and concretionary. Occasionally, botryoidal surfaces of pyrolusite encase hard concentric cores of psilomelane. In lateritic deposits, much of the pyrolusite owes its origin to surface-oxidation products of crystalline schists high in manganese

silicate and carbonate minerals. In such cases, it is frequently found replacing the manganese-bearing mineral along fractures and mineral contacts or following cleavage lines.

Pyrolusite replaces manganosite, manganite, psilomelane, hausmannite, braunite, rhodonite, and rhodochrosite. It is replaced by braunite and psilomelane.

Manganite ($\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$).—Manganite generally occurs as groups of radiating needles or fibers that line druses and cavities, and it is conspicuously developed along contraction fractures in nodules of psilomelane. Concretionary manganite may build

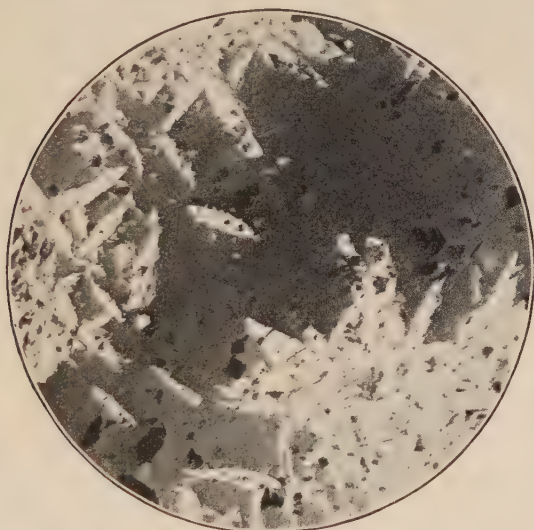


FIG. 1.—Pyrolusite (after manganite) and quartz (dark gray) showing contemporaneous deposition. Bonnet-Hill Mine, Virginia $\times 70$.

up nodules a foot or more in diameter, which are composed of concentric layers of needle-like crystals of the mineral. The layers vary in thickness from less than a millimeter to several centimeters, and in each layer a different arrangement of crystals may be expected. Three different types are common: (1) layers of varying thickness with individual needles extending across the entire width of the layer; (2) needles about $\frac{1}{2}$ centimeter in length, with their axes parallel and dovetailed to build up a layer an inch or more in thickness; (3) short, delicate fibers in an irregular arrangement forming a feltlike layer. The last type is generally present as very thin lamellae between the

other two. In some cases, nodular manganese ore contains nodules the inner core of which is composed of a dense mass of fine manganite needles around which psilomelane is arranged in concentric layers.

Manganite replaces psilomelane, rhodonite, and rhodochrosite. It is commonly replaced by pyrolusite.

Psilomelane ($4\text{MnO}_2(\text{Mn, Ba, K, Co, Ni})\text{O}$).—Psilomelane is widespread in its distribution and is associated with all of the other oxides of manganese. It is commonly massive or in botryoidal, reniform, or stalactitic masses that are concentrated as replacements in many types of rocks and minerals. It owes its origin to the alteration of all the other oxides of manganese, or to direct precipitation as psilomelane. Because of its non-crystalline character, no characteristic sections of mineral grains or outlines of crystal forms can be expected under the microscope.

Where concretionary masses occur as replacements, the concentric structure of psilomelane is conspicuously developed. Frequently, alternating layers show variations in the degree of polish, indicating layers of varying hardness. Since there are several varieties of psilomelane with varying water content, one may assume that the softer layers represent the more hydrous varieties.

Nodular psilomelane has irregular or radial contraction cracks filled with a later generation of the same mineral, or often the fractures are filled with brilliant needles of manganite, which gives the ore a brecciated appearance. In some cases, the structure resembles that of septaria, in which the cracks are filled with psilomelane of a greater hardness which takes a better polish and is, therefore, conspicuous on a polished surface. In nodular ore, concentric layers of psilomelane may alternate with other minerals. Among those observed are manganite, pyrolusite, hausmannite, haeterolite, chalcophanite, limonite, quartz, calcite, siderite, and barite.

Where psilomelane occurs as fine, disseminated grains in an intimate mixture with hausmannite or braunite, or as an alteration product of manganite or pyrolusite, no diagnostic texture is evident, but it is readily identified by its hardness and by microchemical reactions. In some districts, psilomelane replaces hausmannite, and the psilomelane is, in turn, replaced by



FIG. 2.—Alternating layers of psilomelane (white) and calcite (gray) in concretionary replacement. Portsmouth Mine, Cuyuna Range, $\times 80$.



FIG. 3.—Contraction cracks in nodular psilomelane filled with harder psilomelane of a later generation. Bell Mine, Virginia $\times 60$.

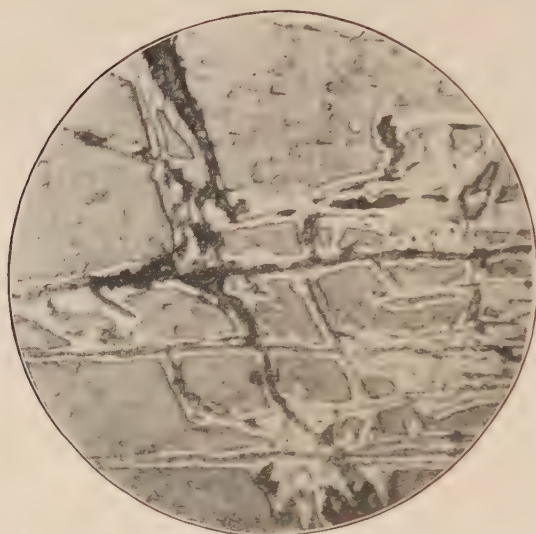


FIG. 4.—Psilomelane replacing a manganiferous pyroxene. Replacement following cleavage. Anderson County, North Carolina $\times 70$.

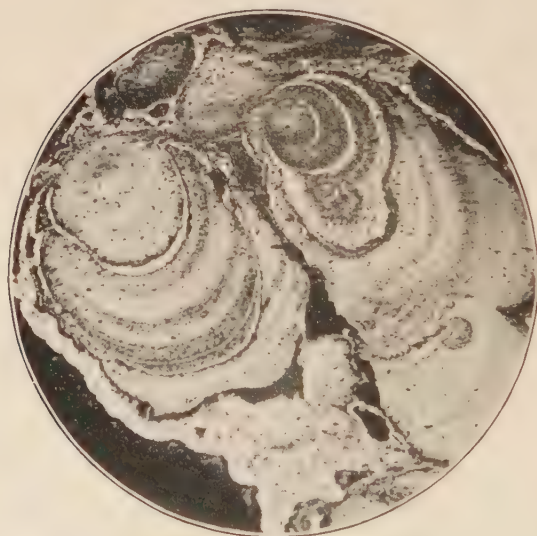


FIG. 5.—Concentric deposition of psilomelane with layers of varying hardness. Difference brought out by slight etching. Craig County, Virginia $\times 70$.

braunite. In the last step, the process may simply be recrystallization with the addition of silica.

Psilomelane replaces or is produced by an alteration of pyrolusite, manganite, hausmannite, braunite, rhodonite, and manganese carbonates and silicates. It is replaced by braunite and pyrolusite. It also alters to wad; and the reverse reaction has likewise been suggested.

Braunite ($3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_2$).—Braunite most commonly appears granular on polished surface because of its tendency to

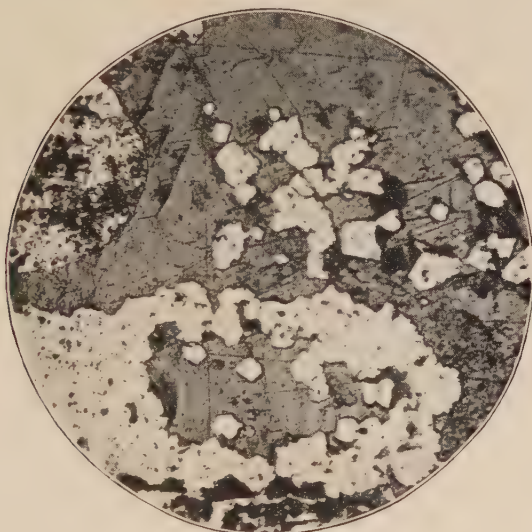


FIG. 6.—Braunite (light gray) replacing calcite, showing the origin of the granular texture that is characteristic of braunite. Batesville, Arkansas $\times 65$.

form small, euhedral, octahedron-like crystals. Because of its marked crystalline character, contacts of braunite with carbonate or silicate gangue minerals that are being replaced show sharp angular *saw tooth* textures where the tetragonal grains penetrate and replace the gangue. Braunite with rhombohedral cleavage has been reported, but it is possible that such structures are pseudomorphic after a carbonate. Euhedral tetragonal crystals, however, are most commonly developed where braunite replaces manganese calcite. The same texture is found where braunite replaces quartz, barite, or rhodonite and, also, where braunite is formed by the recrystallization of hausmannite, psilomelane, and pyrolusite. Where hausmannite, psilomelane,

and braunite are associated, the order of deposition is the order as stated, with a second generation of psilomelane as an alteration of the braunite along fractures and contacts of mineral grains. Braunite and psilomelane are also found where rhodinite and rhodochrosite have been subjected to oxidation.

Braunite may be found in the following associations: (1) with the products of crystallization of an igneous intrusive; (2) with the products of metamorphism of manganese sediments; (3) with the products of alternation of manganese silicates, such as manganese—garnets and pyroxenes.

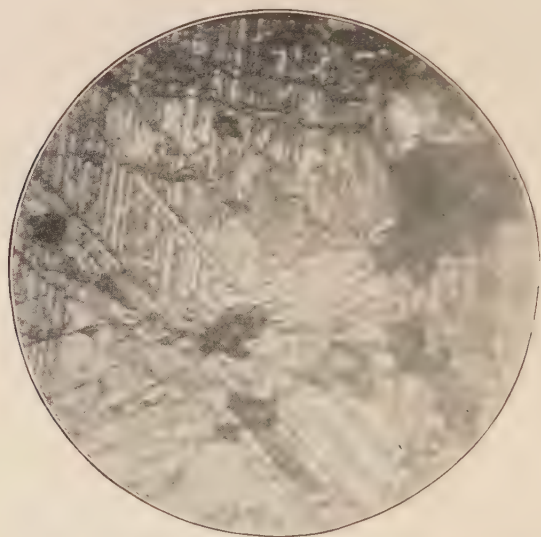


FIG. 7.—Etch pattern of hausmannite. Batesville, Arkansas $\times 65$.

Hausmannite (Mn_3O_4).—Hausmannite was formerly considered a rare manganese mineral, but microscopic studies of associated manganese oxides reveal its presence in many districts and with a variety of other manganese minerals. Coarsely crystalline hausmannite exhibits conspicuous crystallographic structures on polished surface, after treatment with a drop of hydrogen peroxide or dilute sulphuric acid. It is found associated with braunite and psilomelane, especially as replacements in limestone rocks. Because of its lower oxygen content, its formation is considered as taking place where the supply of available oxygen is limited. In the Batesville district, most of

the hausmannite occurs in an intimate mixture disseminated through compact psilomelane. Gradations are evident from massive psilomelane with a few grains of hausmannite scattered through it, to a coarse, granulated hausmannite with tiny specks of psilomelane.

In some regions, hausmannite is associated with manganiferous carbonates as intimate intergrowths in delicate plumose masses. The oxide occurs as minute octahedral crystals on the borders of the carbonate grains or as a drusy lining for minute cavities or fissures.

Hausmannite replaces manganiferous carbonates and is, in turn, replaced by braunite, psilomelane, and pyrolusite. It also shows intergrowths with psilomelane which indicate contemporaneous deposition.

Alabandite (MnS).—The manganese sulphide, alabandite, should be included in a list of the opaque manganese ores; but its origin and, consequently, its associations are quite different from those of the oxides. It occurs as a primary-vein mineral with metallic sulphides, and it is, therefore, associated with minerals of copper, silver, lead, zinc, etc. It is readily detected on polished surface by its green internal reflection with inclined light and its olive-green powder when scratched. Acids which attack it liberate hydrogen sulphide.

The Relations of Manganese and Iron Oxides in Manganiferous Iron Ores.—In many districts, manganese oxides are intimately associated with iron oxides in the form of manganiferous iron ores. The following relations are found in polished surfaces of such ores:

1. Simultaneous replacement of chert by manganite and hematite.

2. Contemporaneous deposition of hematite and psilomelane in nodular concretionary ores as alternating microscopic layers.

3. The replacement of stalactitic and concretionary limonite by manganite.

4. An intimate intergrowth of manganite and pyrolusite with hematite in martite grains.

5. Finely laminated pyrolusite and limonite as products of oxidation of thinly laminated sediments.

Massive, yellowish-brown, manganiferous ore, when polished, shows an intimate mixture of hematite, limonite, manganite, and psilomelane with a textural relation denoting the contem-



FIG. 8.—Radiating groups and irregular masses of manganite needles in a concentric layer of concretionary ore. Cuyuna Range. $\times 60$.

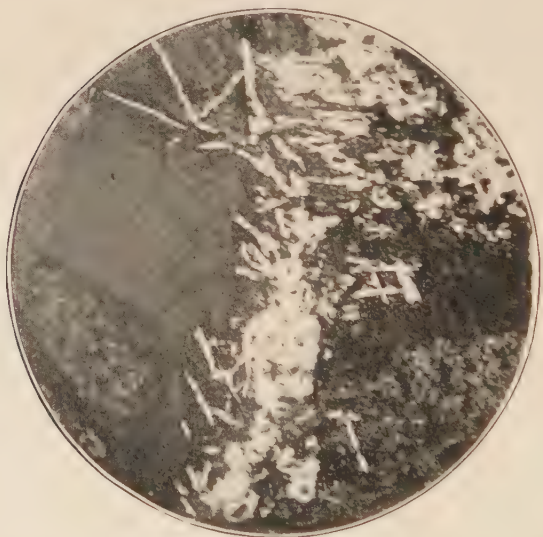


FIG. 9.—Manganite needles replacing carbonate minerals, showing a tendency to follow cleavage lines. Cuyuna Range. $\times 65$.

poraneous deposition of some of the oxides. The relation of the manganite needles to limonite and hematite indicates that limonite and manganite can be deposited simultaneously. Of the iron oxides in such ore, limonite appears to be deposited

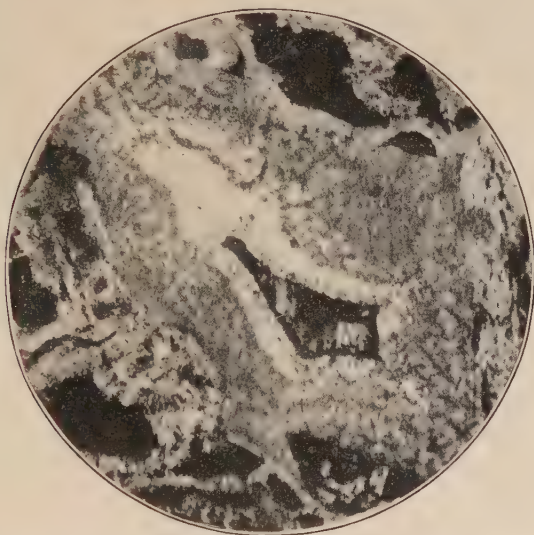


FIG. 10.—Intimate mixture of hematite (white) and manganite (gray) replacing calcite (etched black). Hillcrest Mine Cuyuna Range, $\times 80$.

earlier than hematite, for hematite replaces needles of limonite which are replacements of manganiferous and ferriferous calcite, ankerite, and groups of fibrous amphiboles derived from the original rock minerals.

CHAPTER X

GEOLOGIC THERMOMETRY

BY N. L. BOWEN¹

Introduction.—A knowledge of the conditions of formation of minerals, the temperatures, pressures, and concentrations involved, is a matter of much importance to the student of ore deposits, both theoretically and practically. Information regarding the formation of ore minerals may be gleaned not merely from known facts concerning ore minerals themselves but from facts concerning any minerals which may be associated with the ore minerals in such a way as to offer evidence of the relative conditions of formation. The problem of the temperature of formation of ore minerals can thus be adequately treated only as a part of the more general problem of mineral formation.

SOURCES OF INFORMATION

On this problem, information is to be had from two sources:

1. Direct observation and measurement of temperatures.
2. Deduction based on ascertained facts regarding the effect of temperature on various physical properties of minerals and physicochemical properties of mineral systems.

The first of these sources is, of course, much to be preferred but, in the nature of the case, is not commonly available. Nevertheless, much useful information has been obtained by measurement of temperatures of lavas, of volcanic gases, and of various kinds of springs.

TEMPERATURE OBSERVED DIRECTLY

Lava Flows.—The highest temperatures of geological phenomena which come under direct observation are those of lava outpourings. Occasionally, these have taken place under conditions which permit the measurement of the temperature of

¹Turned in for publication in May 1926 so that adequate notice, or usually any notice of subsequent papers has been impossible. N. L. B.

the lava. The earlier methods of measurement, while giving valuable indications, were not always of great reliability. They depended upon observing whether the temperatures were adequate to melt wires of various metals inserted in the lava and were naturally somewhat vitiated by the existence of chemical corrosion. More recent measurements by thermoelectric and optical methods have given reliable values. Temperatures as high as 1185° have been measured in the lava lake of Kilauea.¹ At Vesuvius, temperatures from 1015 to 1040° have been observed.² Though the lavas of both these volcanoes are basic, they are of very different characters, the one being a normal basalt and the other, a leucite tephrite.

Eruptions of acidic lavas are usually of so explosive a character that little opportunity is presented for making measurements of temperature. H. S. Washington estimates, from its color, that the temperature of the hottest visible lava at Santorini during the 1925 eruption³ was between 800 and 900° . The lava is a dacite of approximately 65 per cent silica content. A distinctly lower temperature than that of basic lavas is indicated.

The significance of these figures in connection with the problem of ore formation is that they constitute a maximum temperature above which rocks brought into contact with magmas cannot safely be assumed to have been raised. Presumably, there are hotter magmas at very great depths, but their temperatures have more to do with general cosmic problems than with the practical problems of mineral deposition. A rapidly extruded lava probably arrives at the surface with sensibly the same temperature as it had in the place of its origin and practically as high as any that are concerned with mineral formation in those parts of the crust which are ever exposed in artificial or natural sections. Any mineral transformations which may be brought about in thermocontact metamorphism must have taken place at temperatures lower than these and, in most cases, considerably lower. And, further, any mineral transformations or introduction of minerals which are later than these contact transformations and which may be safely assumed

¹ Measured by Perret, Day, and Shepherd. Higher temperatures are noted where marked combustion of gases occurs. See JAGGAR, *Am. Jour. Sci.*, Vol. XLIV, p. 214, 1917.

² PERRET, "The Vesuvius Eruption of 1906," *Carnegie Inst. Pub.* 339, p. 132.

³ Personal communication.

to belong to the same cycle of activity must, ordinarily, be assigned to still lower temperatures.

Fumaroles.—In addition to lava temperatures, the other elevated temperatures which can be directly measured are those connected with what may be termed the *waning phases of volcanism*. Emanations from magmas appear at the surface in forms which have been designated under various terms, including fumaroles, soffioni, moffetas, geysers, and hot springs. Many of these have been studied, their temperatures measured, and the nature of the material transported and deposited by them ascertained. From these observations, some valuable information has been obtained as to the nature of the solutions and temperatures concerned in mineral formation.

Gases emitted from flowing lava have, no doubt, the temperature of the lava itself. In positions more removed from the center of activity, and in periods of waning activity, lower temperatures obtain. A gas temperature as high as 645°C . has been measured in the fumaroles of Katmai. A temperature of 560°C . has been noted in a Vesuvian fumarole.

A great number of substances may be deposited from fumarole gases, including various chlorides, such as those of sodium, potassium, and ammonium and, among the heavy metals, of iron and lead. In addition, sulphides such as realgar, cinnabar, and galena may be observed, and various complex compounds of copper, zinc, manganese, and other elements. There is frequently much boric acid and, at times, various fluorides. Zies has made an interesting study of the magnetite deposits of the Katmai fumaroles and suggests that they were formed by hydrolysis of halogen compounds of iron.¹

The change of temperature and pressure conditions is so rapid in a gas thus escaping freely into the atmosphere that little is to be learned concerning the temperatures of deposition of the various substances. It is especially to be noted that no very close analogy can be drawn between the substances so deposited and those formed more slowly under deeper-seated conditions where a closer approach to equilibrium may be expected.

The principal information furnished is with reference to the nature of the material which can be given off by magmas and, therefore, may be introduced into surrounding rocks.

¹ ZIES, E. G., "The Fumarolic Incrustations in the Valley of Ten Thousand Smokes." National Geographic Soc., Contributed Technical Papers, Katmai series, No. 3, 1924, p. 179.

No important generalizations have been reached upon the variation of the emanations with temperature. Some have believed that the gases given off at high temperatures tend to be rich in chlorides, while at lower temperatures sulphides become more important. If this be true, the commonly observed succession in contact metamorphism may find its explanation therein. The sulphides are ordinarily preceded by oxides, which may, perhaps, be regarded as formed by the hydrolysis of halogen compounds.

Against the general truth of this condition is the fact that, at Kilauea, gas taken directly from the liquid lava was sometimes rich in sulphur compounds but entirely free from chlorine. It is probable, therefore, that the stage of evolution or differentiation of the magma itself from primordial magma requires to be considered before any generalization is likely to be found regarding the composition of volatile matter that may be given off at different temperatures.

Hot Springs.—The subject of hot springs is one of great magnitude and variety. Here can be given no more than a brief suggestion of their importance in connection with the general problem of thermometry. Many minerals are deposited only at moderate temperatures and under near-surface conditions. Hot springs thus furnish an opportunity for the study of mineral deposition under conditions that approach the normal for this particular class of deposit.

The distinction between the hot spring and the fumarole is fixed by the boiling point of water. This varies, of course, with pressure, so that what is a fumarole at the surface may be of the nature of a hot spring in depth. For the general problem of mineral transport and deposition the boiling point of water under surface conditions has, therefore, no special significance.

The temperatures of springs vary from the boiling point of water (or, perhaps, slightly higher when the solutions are strong) to the ordinary temperature, and they therefore throw some light on the nature of the solutions concerned in the deposition of minerals at such temperatures. Among the observed minerals of spring deposits, opal, chalcedony, quartz, calcium carbonate, and limonite form the bulk of the material. Barite, gypsum, and other sulphates, fluorite, and some zeolites are well-recognized species in such deposits. Among metallic minerals are cinnabar, realgar, orpiment, and stibnite, which

are confined to low-temperature deposits, and pyrite, which can occur in deposits of high temperature as well.

DEDUCTION OF TEMPERATURES OF DEPOSITION FROM THE INHERENT PROPERTIES OF MINERALS AND MINERAL ASSOCIATIONS

General Considerations.—We have seen that there are many examples of mineral deposition taking place in accessible positions and, thus, affording opportunity for measurement of the conditions of deposition. The facts thereby ascertained, however, usually find their greater usefulness in furnishing information as to the nature of materials which are concerned in ore formation and as to the forms of combination in which these materials are transported. For information concerning the temperatures of deposition of minerals under the normal conditions obtaining in depth, principal reliance must be placed upon other considerations. In fact, the conditions of deposition must, as stated before, be deduced from data upon the physical and physicochemical properties on minerals and mineral systems, especially the variation of these properties with temperature and, to some extent, with pressure, for their effects are not mutually independent.

If the temperature of a crystalline substance is raised, it will eventually reach a value where the substance suffers a change of form, and this change then permits a definite limit to be placed upon the region of stable existence of the substance as originally constituted. This *change of form*, as it is called above, may be of various types. The substance may dissociate into more than one crystalline substance. It may dissociate into one or more liquids and one or more crystalline substances. It may dissociate into a gas and one or more crystalline substances. On the other hand, the substance may suffer no dissociation at all but may simply invert to another crystalline form; or, again, it may do none of these and simply melt as such or, perhaps, sublime if the pressure is inadequate to insure melting. Such of these changes as a substance may undergo take place at a definite temperature or through a definite range of temperature, depending on the complexity of the change; in the language of the *phase rule*, depending on the number of phases involved as compared with the number of components. Pressure affects the temperature of any of the changes which may occur. The

direction and magnitude of the effect of pressure depends directly on the direction and magnitude of the change of volume and inversely upon the magnitude of the heat effect. Where all the phases involved are liquid or solid, the effect of pressure upon the temperature of the change is moderate, because the volume change is moderate; but where one of the phases is a gas, the effect of pressure is very great.¹

The presence of another substance affects the temperature of any of the possible mentioned changes in a given substance, if, and only if, the other substance can enter into the composition of one or more of the phases involved in the change. Thus, the melting point of a silicate is always changed by the presence of another silicate, because the liquid formed always contains some of the other silicate. On the other hand, the melting temperature of a silicate remains unaffected in the presence of platinum because platinum enters into the composition of neither the liquid nor the solid phase. An inversion temperature or a (solid) dissociation temperature may remain unaffected in the presence of other substances, if the other substances do not enter into the composition of any of the solid phases concerned. Thus, the inversion temperature of quartz to tridymite is unaffected by the presence of other substances, because neither takes other substances into (solid) solution. On the other hand, the inversion temperature of wollastonite is affected by the presence of magnesium metasilicate, because wollastonite takes magnesium metasilicate into solid solution. Likewise, the inversion temperature of pyrrhotite is changed by the presence of pyrite, because pyrite (or S) is taken into solid solution.

If, for all natural substances and mixtures thereof, the magnitude of the effects of these several factors upon the various phase changes were determined, we should be able to place definite

¹ The exact equation expressing the effect of pressure upon any equilibrium phase change (boiling, melting, inversion, dissociation) is the Clausius-Clapeyron equation:

$$\frac{dt}{dp} = \frac{T(v_1 - v_2)}{l}$$

where dt is the change of the temperature at which the phase transformation occurs produced by a change of pressure dp . T is the absolute temperature, l is the latent heat of the change, and $v_1 - v_2$ is the change of volume.

limits upon their regions of stability. There would, thus, be at hand a wealth of information upon which might be based conclusions concerning the conditions of their genesis in nature. Unfortunately, the factors involved are quite unknown, in the great majority of cases. The phase changes which may be put to use must, therefore, be those of a comparatively simple kind, preferably those taking place in a single phase and either unaffected by the presence of other phases or affected in a known way.

Melting Points.—The melting point of any crystalline substance places an upper limit upon the temperature range in which that substance can crystallize. To be sure, this is frequently not a particularly useful fact, for the presence of other substances usually lowers the melting point so much that the limitation placed by the melting point of the substance itself is altogether too wide. Nevertheless, useful deductions can, at times, be drawn, and it may be well to recall some determined melting temperatures, especially those of particular significance in the present connection (see Table I).

TABLE I.—SIGNIFICANT MELTING POINTS OF MINERALS

Olivine ¹ (forsterite) (Mg ₂ SiO ₄).....	1,890	Jamesonite ⁶ (2PbS.Sb ₂ S ₃).....	609*
Enstatite ¹ (clinoenstatite) (MgSiO ₃)...	1,557*	Plagionite ⁶ (5PbS.4Sb ₂ S ₃).....	570*
Plagioclase ² (An) CaAl ₂ Si ₂ O ₈	1,550	Stibnite ⁶ (Sb ₂ S ₃).....	546
Diopside ³ (CaMgSi ₂ O ₆).....	1,391	Miargyrite ⁶ (Ag ₂ S.Sb ₂ S ₃).....	509
Plagioclase ² (Ab) (An).....	1,287-1,450	Pyrargyrite ⁶ (3Ag ₂ S.Sb ₂ S ₃).....	483
Orthoclase ⁴ (KAlSi ₃ O ₈).....	1,170*	Calaverite ⁷ (AuTe ₂).....	472
Plagioclase ² ((Ab)NaAlSi ₃ O ₈).....	1,100	Orpiment ⁸ (As ₂ S ₃).....	320
Pyrrhotite ⁵ (FeS + S).....	1,157-1,187	Realgar ⁸ (AsS ₃).....	310
Galena ⁵ (PbS).....	1,120	Bismuth ⁹ (Bi).....	271
Argentite ⁶ (Ag ₂ S).....	842	Sulphur ¹⁰ (S).....	119

* The minerals marked thus melt incongruently.

¹ BOWEN and ANDERSEN, *Am. Jour. Sci.*, Vol. XXXVII, pp. 487-500, 1914.

² BOWEN, *Am. Jour. Sci.*, Vol. XXXV, p. 582, 1913.

³ DAY and SOSMAN, *Am. Jour. Sci.*, Vol. XXXI, p. 345, 1911.

⁴ MOREY and BOWEN, *Am. Jour. Sci.*, Vol. IV, p. 1-21, 1922.

⁵ ALLEN, CRENSHAW, JOHNSTON, and LARSEN, *Am. Jour. Sci.*, Vol. XXXIII, pp. 169-236, 1912.

⁶ JAEGER and VAN KLOOSTER, *Z. anorg. Chem.*, Vol. LXXVIII, pp. 245-268, 1912.

⁷ PELABON, *Compt. rend.*, Vol. CXLVIII, p. 1,176, 1909.

⁸ BORGSTRÖM, *Översigt Finsk. Videnskab-Soc. Forh.*, Vol. LVII, pp. 1-13, 1914-1915.

⁹ JOHNSTON and ADAMS, *Am. Jour. Sci.*, Vol. XXXI, p. 517, 1911.

¹⁰ WIGAND, *Z. physik. Chem.*, Vol. LXV, p. 65, 1908.

Though many exceptions are to be noted, especially among minerals not here listed, there is, nevertheless, a general tendency displayed in mineral melting point. It is that the minerals of basic rocks are of higher melting point than those of acid rocks.

These are, in turn, higher than the melting points of the simple sulphides. The simple sulphides of the heavy metals, again, melt at a higher temperature than the complex sulphides or sulpho salts. The fact that the general succession of the minerals in rocks and ore deposits is in the same order and that this represents an order of falling temperatures is not unconnected with this descending series of melting points.

As an example of the manner in which the melting point of a substance may be used as an indication of maximum temperature, it may be pointed out that the native bismuth of the Cobalt silver deposits and any minerals which are known to be essentially contemporaneous with or later than the bismuth must have been deposited at a temperature below 271° .¹ Bastin has concluded that there is an overlapping of the various episodes of mineral deposition at Cobalt.² If there is no significant time break, there may have been no great temperature difference, and it is possible that the whole mineralization is to be referred to temperatures below, say, 250° .

On a later page, an example is given in which the melting point of jamesonite is put to use.

The melting temperatures of assemblages of substances would, of course, be more useful for setting a maximum temperature of crystallization of the assemblage. Usually, however, it is just this kind of knowledge that is lacking (namely, knowledge of changes involving a number of phases). We must ordinarily, therefore, rely on determined facts regarding individual substances or phases. In a few cases, however, pertinent observations have been made. A eutectic between galena and argentite has been determined at 630° ; between plagioclase and stibnite, at 485° . Pyargyrite and proustite are said to form a complete series of solid solutions at high temperatures with a minimum melting point at 473° .³ Since they are found in nature side by side as distinct phases, these solid solutions must unmix at lower temperatures, and the natural minerals are, presumably, formed

¹ It is worthy of note that bismuth, unlike most substances, contracts on melting and that its melting point is, therefore, lowered by increased pressure. At 3,000 atmospheres, corresponding with a depth of nearly 10 kilometers in the earth, it is lowered only to 260° . BRIDGMAN, *Phys. Rev.*, N. S., Vol. VI, p. 27, 1915.

² BASTIN, E. S., *Econ. Geol.*, Vol. XX, p. 14, 1925.

³ JAEGER and VAN KLOOSTER, *Z. anorg. Chem.*, Vol. LXXVIII, p. 267, 1912.

below the unmixing temperature. This temperature has, however, not been determined.

The eutectic between silver and bismuth is at 262° , a fact which fixes a maximum temperature for the formation of bismuth in the presence of silver (as at Cobalt) at a slightly lower value than does the melting point of bismuth.

It is not very likely, however, that eutectics play a dominant role in the equilibria governing mixtures of ore minerals any more than they do in the silicate minerals. Thus, it is found that there is no eutectic between galena and jamesonite and, again, none between jamesonite and pligionite. The relation among these three is what has been termed a *reaction relation*.¹ Thus, it is not to be expected that jamesonite and galena will be found crystallized in such a way as to indicate that jamesonite crystallizes first when very abundant and galena first when the opposite condition prevails, each being followed by a simultaneous eutectic crystallization of the two. On the contrary, it is to be expected that in a normal cooling sequence jamesonite will always follow galena and will bear a reaction (attacking) relation to the galena, similar to that obtaining between olivine and pyroxene in rocks. A like relation is to be expected of pligionite with respect to both jamesonite and galena. Even though they are formed from solutions rather than from melts, this relation is not likely to be changed.

INVERSION POINTS

Quartz, Tridymite, and Cristobalite. The inversion points of crystalline substances are the most useful reference points we have in geologic thermometry. For a number of reasons, the most important substance from this point of view is silica. It occurs in several different crystalline forms whose stability ranges are known. It is of widespread occurrence. In all of its crystalline forms it is of remarkable purity; in other words, it takes no significant amount of any other substance into solid solution, and we need not concern ourselves, therefore, about variation of the inversion points from that cause.

Four stable crystalline modifications of silica are known: (1) high cristobalite, (2) high tridymite, (3) high or β -quartz, and (4) low or α -quartz. Both cristobalite and tridymite have

¹ BOWEN, N. L., "The Reaction Principle in Petrogenesis," *Jour. Geol.*, Vol. XXX, pp. 177-198, 1922.

metastable inversions at low temperatures, but the low-temperature forms have no importance in the present connection. The stable inversions of silica are as follows:

α -quartz \rightarrow β -quartz.....	573°C.
β -quartz \rightarrow tridymite.....	870°C.
tridymite \rightarrow cristobalite.....	1470°C. ¹

The effect of pressure upon the various inversions of silica can be calculated by substituting in the Clausius-Clapeyron equation (p. 177) the values of the quantities concerned. For the α - β -quartz inversion, it is difficult to decide just what values of the volume change and heat effect should be used, for there is, in both cases, a marked pre-inversion effect, and it is not certain how much of this is part of the essential thermodynamics of the inversion. Since, however, they appear in the equation as a ratio, the inclusion of too much or too little of both may not seriously affect the result. Taking, therefore, the whole volume change from 550 to 585°, which is 0.0056 cubic centimeter per gram,² and the whole heat effect, which is approximately 5 calories,³ we find that 1,000 atmospheres' pressure should raise the inversion point a little more than 20°.⁴

Applying the same considerations to the inversion quartz \rightarrow tridymite, and using the best data available, we find that the effect of 1,000 atmospheres' pressure should be to raise the inversion point an amount in the neighborhood of 100°. This pressure corresponds with a depth of nearly 2½ miles in the crust.

No precise significance can be attached to either of these values. They serve merely to indicate the order of magnitude of the change of inversion in so far as it can be predicted in the present state of knowledge.

Throughout the present discussion, when the temperatures 573 and 870° are spoken of as *fixed points*, it is to be understood

¹ The most exhaustive study of the transformations of silica has been made by FENNER, *Am. Jour. Sci.*, Vol. IV, No. 36, pp. 331-384, 1913.

² DAY, SOSMAN, and HOSTETTER, *Am. Jour. Sci.*, Vol. XXXVII, p. 16, 1914.

³ Estimated from the specific-heat data of W. P. White.

⁴ Since this was written the change of inversion has been determined by Gibson of the Geophysical Laboratory and found to be 21.5° for the first 1,000 atmospheres.

that these values require correction for the pressure concerned, and the above discussion is introduced in order to convey some idea of the order of magnitude of this correction. For the present rough purposes of geologic thermometry, it is plain that the effect on the α - β -quartz inversion need cause no concern. The effect on the quartz-tridymite inversion is, however, such that for great depths we must bear in mind that a considerable raising is to be expected.

The stable inversions of silica are not all of like character. The α - β -quartz inversion takes place promptly upon passing through the temperature of the inversion point in either direction. The other two inversions, on the contrary, may be readily overstepped in either direction. Thus, it comes about that tridymite and cristobalite may be found in rocks at ordinary temperatures, although they are unstable at these temperatures, but quartz at ordinary temperatures is always α -quartz. Not only may tridymite and cristobalite persist at temperatures outside their range of stable existence, but they may actually form at these temperatures. Indeed, it has been observed in a number of silicates with inversion points that the modifications stable at high temperatures may be formed at low temperatures. On the other hand, it has not been observed that low-temperature forms may originate at high temperatures, and this may, with a high degree of safety, be taken as a general rule and be applied to their formation in nature. We may, therefore, say that cristobalite can form at *any* temperature below 1713° ; tridymite, at *any* temperature below 1470° ; and quartz, at *any* temperature below 870° . Of these three facts, it is plain that the only one of any general utility is the last, namely, the fact that quartz forms only below 870°C .

There are certain instances, however, in which the presence of cristobalite or tridymite may have definite temperature significance. These are occurrences in which it can be demonstrated that tridymite or cristobalite was formed directly by the inversion of quartz. Here we know that the quartz was heated to a temperature above 870° ; but if the new form is cristobalite we may not safely infer that it was heated above 1470° . In applying this criterion to determine a temperature above 870° , we must be very sure that we are dealing with simple inversion of the quartz and not with solution and reprecipitation of silica, for the reprecipitated silica might assume the form of tridymite

or cristobalite even though the conditions were those in which quartz was stable.

It must be recalled, moreover, that the fact that silica occurs as quartz in a given sample does not necessarily mean that the silica assumed crystalline form entirely below 870° . It is possible that the silica was first individualized as tridymite or cristobalite, which later changed to quartz on cooling; for, if the cooling is sufficiently slow, tridymite and cristobalite may not persist when cooled to ordinary temperatures. Quartz so formed, however, can usually be recognized as such, and only rarely is this fact of importance.

α -quartz and β -quartz.—In addition to the 870° point furnished by quartz, the 573° point corresponding with the α - β -quartz inversion is of much importance. As has been stated before, all quartz at ordinary temperature is α -quartz; but some examples were formed as such, whereas others were formerly β -quartz and have inverted to the α form upon cooling. The question whether a given crystal grain of quartz was formed above or below 573° can be definitely decided if we can tell whether or not it has suffered inversion. The changes which occur in quartz at the inversion point have been studied by a number of observers, among them Mallard and Le Chatelier,¹ Mügge,² and Wright and Larsen.³

The last-mentioned authors state four criteria which can be used to distinguish quartz which was formed above 573° from quartz which has never been heated to that temperature:

(1) Crystal form, if crystals be available, the presence of trigonal trapezohedrons and other evidence of tetartohedrism, irregular development of the rhombs and the like, being indicative of the α -form. (2) Character of twinning, as shown by etch figures on the basal pinacoid. In the α -form, which crystallized from solutions at comparatively low temperatures, the twinning is usually regular and sharply marked, while in quartz plates originally of the β -form and now α by virtue of inversion in the solid state, the lines are usually irregular, and the twinning patches are small and bear no relation to the outer form of the crystal. (3) Intergrowths of right- and left-handed quartzes are more

¹ MALLARD and LE CHATELIER, *Bull. Soc. Min. Fr.*, Vol. XIII, p. 123, 1890.

² MÜGGE, O., *Neues Jahrb. Festband*, pp. 181-196, 1907; *Centralbl.*, p. 609, 1921.

³ WRIGHT, F. E., and E. S. LARSEN, *Am. Jour. Sci.*, Vol. XXVII, pp. 421-447, 1909.

frequent and more regular in boundary lines in the α - than in the β -form. (4) Plates of originally β -quartz but now α -quartz by inversion show the effect of the inversion by the shattering which should be most evident on large plates.

It will be noted that all four criteria, except, in some cases, the crystal form, are concerned with tendencies rather than with any sharply distinctive feature. It is not usually possible, therefore, to reach an unequivocal decision for any individual sample of quartz. Ordinarily, only the probabilities of the case can be stated. If examination is extended, however, to a large number of samples of quartz whose geological occurrence indicates community of origin, and if all or nearly all of these have characters which point in the one direction, then the probability becomes very great that quartz of such an origin is formed under the conditions indicated by these characters. Wright and Larsen examined 10 specimens of quartz from veins, 21 from pegmatites, and 13 from granites and granite porphyries. They were led to conclude that

. . . vein and geode quartzes and certain large pegmatite quartz masses and pegmatite veins were formed below 575° , while graphic and granite pegmatites and granites and porphyry quartzes were in all probability formed above 575° .

Wollastonite and Pseudowollastonite.—Another inversion point of considerable importance in connection with the temperatures of geologic processes is that of CaSiO_3 , which exhibits the two forms—wollastonite and pseudowollastonite—with a transformation point at 1180° . Pseudowollastonite, the form stable above 1180° , has never been found in nature. The inversion point is raised by the presence of MgSiO_3 , and when a sufficient quantity of that substance is present, it may occur only above 1300° . Nevertheless, there are unquestionably many examples of siliceous limestones nearly free from magnesia that have suffered thermal metamorphism. The complete absence of natural pseudowollastonite must, therefore, be regarded as signifying that magmas seldom if ever heat their wall rocks or even immersed inclusions to a temperature of 1180° . The question whether some wollastonite is not a paramorph after pseudowollastonite cannot be answered categorically, perhaps, but it is unlikely that if this were commonly true it would have escaped

detection. It does not seem probable, therefore, that the general conclusion will require revision on that score.

The 1180° point is, of course, more useful for the determination of magma temperatures than for the fixing of temperatures of mineral changes connected with ore formation. The limitations upon conditions of even the most extreme of these changes, *viz.*, thermal metamorphism, are much more rigidly drawn by the fact of the usual presence of quartz and absence of tridymite or cristobalite—a temperature below 870°C. being, thus, ordinarily indicated.

Pyroxene, Hornblende, and Chlorite.—The statement is occasionally encountered in the literature that the inversion point between pyroxene and hornblende is at 550°C. and 200 atmospheres' pressure. This conclusion comes, not directly but by rather devious channels, from some early experiments by Chrustschoff, who claimed to have made hornblende hydrothermally at 550° in glass containers.¹ In the first attempt to use Chrustschoff's result, it was pointed out merely that a stability range for pyroxene above 550° was indicated. Each successive author has made the statement more definite, until, finally, it has assumed the present form of giving an exact inversion point at 550°, with a definite pressure of 200 atmospheres gratuitously added. As a matter of fact, no one has been able to duplicate Chrustschoff's experiments, and they must be regarded as of doubtful validity. In any case, it is plain that they offer no warrant for the conclusion now drawn; indeed, it must be admitted that we have, on this matter, absolutely no information that can be safely used even for the simplest pyroxene or amphibole, much less for the groups as a whole. Given corresponding pressure conditions, we may, however, obtain valuable indication of relative temperatures on the basis of the presence of pyroxene on the one hand and of hornblende on the other. The latter points to a lower temperature, and a still lower temperature is indicated by chlorite, but we have no information that would warrant the assignment of any definite temperatures to any of them.

Sphalerite and Wurtzite.—Among the common sulphides, that of zinc occurs in two forms with an inversion point at 1020°, the hexagonal wurtzite being stable above that temperature and

¹ *Compt. rend.*, Vol. CXII, p. 677, 1891.

the isometric sphalerite stable below that temperature.¹ Pure sphalerite can form only below 1020°, but wurtzite can form not only at high temperatures but also metastably at low temperatures.² The presence of iron in solid solution lowers the inversion point so that blende with 17 per cent Fe inverts at 880°. These facts indicate that sphalerite can form only at temperatures below 1020° and, when rich in iron (17 per cent), only below 880°. There are, of course, many other facts that point to temperatures far below these as the common temperatures of deposition of sphalerite, but geologic thermometry is a subject in which as much cross-checking as possible should be practiced.

INVERSIONS AT LOWER TEMPERATURES

There is a considerable region of intermediate temperatures (below 575°) where there are no very satisfactory fixed reference points. Our knowledge of temperatures of deposition in this region depends on such determinative features as fluid inclusions in crystals. Undoubtedly, as time passes, serviceable points will be discovered in this range. Inversion points are, in general, much more satisfactory fixed points than any other, because the nature of the solution depositing the mineral cannot affect an inversion point unless some of the substances present in the solution enter into the composition of the crystalline mineral. In such a case, the nature and magnitude of the effect of other substances in solid solution in the crystal can generally be determined, and their significance in connection with any individual deposit approximately evaluated.

Boracite.—The inversion point of boracite at 265° is not of great service, on account of the restricted occurrence of this mineral. The isometric form, stable above 265°, is transformed upon cooling through that temperature into a twinned, birefracting modification. Mügge has concluded, therefore, that the usual crystals of boracite, with isometric external form, must have crystallized above 265°.³ Brauns has questioned this conclusion, pointing out that many modifications of crystalline

¹ ALLEN, CRENSHAW, and MERWIN, *Am. Jour. Sci.*, Vol. XXXIV, p. 347, 1912.

² Acid conditions favor the formation of the metastable wurtzite just as they do that of the unstable marcasite. A like condition has been found in other sulphides, but a full discussion would be out of place here.

³ MÜGGE, O., *Neues Jahrb. Mineral.*, Vol. I, p. 123, 1921.

substances may form at temperatures below their region of stability.¹ This is quite true for some substances; we have already noted the fact for cristobalite and tridymite. But in applying it we must always have regard for the nature of the inversion. The work of Haga and Jaeger indicates that the inversion of boracite is instantaneously reversible like that of α - and β -quartz.² In the case of such an inversion, we have no warrant for believing that the high temperature modification can form below its stable region; indeed, all experience is to the contrary. There would, thus, seem to be no escape from accepting Mügge's conclusion as to the formation of isometric boracite above 265° and from drawing the necessary inference as to the temperatures attained in the salt deposits where it occurs.

Argentite and Chalcocite.—Two sulphides of relatively common occurrence have inversion points which may prove of service in thermometry. They are argentite (Ag_2S) and chalcocite (Cu_2S). Both are isometric above their inversion points but of lower symmetry below that temperature. Argentite has a transformation point close to 175° . At ordinary temperature, its crystals are anisotropic and intricately twinned,³ though faceted crystals are always of isometric external form. It is presumably at the 175° inversion point that the twinned form is assumed, and these characters of argentite appear to indicate its formation above 175° . The matter requires further study, however, especially with reference to the promptness of the inversion as bearing on the possibility of the formation of the isometric modification at a temperature below its stable region. The question whether the natural mineral acanthite is a distinct form of silver sulphide, as well as whether it represents the form stable below 175° , also requires further investigation.⁴

The chalcocite inversion point has received a considerable amount of study. It takes place at approximately 91° . The point may be raised by the presence of CuS in solid solution, but the effect is so small that it is of no practical importance. When more than 8 per cent CuS is present in solid solution, inversion

¹ BRAUNS, R., *Centr. Mineral.*, p. 228, 1921.

² HAGA and JAEGER, *Proc. Acad. Sci. Amsterdam*, Vol. XVI, p. 5, 1914.

³ SCHNEIDERHÖHN, "Anleitung zur Mikroskopischen Bestimmung von Erzen," p. 207, Berlin, 1922.

⁴ RINNE, *Z. Kryst.*, Vol. LX, pp. 299-301, 1924; KALB and BENDIG, *Centr. Mineral.*, p. 516, 1924.

does not occur, the chalcocite remaining isometric upon cooling to ordinary temperatures.¹

Chalcocite is, in all probability, both of supergene and hypogene origin. This low-temperature inversion may be useful in determining the class to which it belongs in any individual deposit, a matter of much practical importance as indicative of the probable extension in depth of this rich copper compound. A temperature of formation above 91° may be taken to indicate hypogene conditions; and a temperature below 91° would, ordinarily, though perhaps not necessarily, indicate supergene conditions. Unless it contains more than 8 per cent CuS, chalcocite is always orthorhombic at ordinary temperature, but if it was originally isometric, that is, was formed above 91°, etching brings out a survival of the octahedral structure. Posnjak, Allen, and Merwin have applied this criterion to the determination of the temperature of formation of various chalcocites.² Bateman has also considered it in connection with two deposits, concluding that the one was formed above 91°³ and the other below that temperature.⁴ In the latter example, however, he still regards the chalcocite as primary or hypogene, so that the low temperature of its formation is not, in this case, taken as indicative of supergene origin.

Monotropic Substances.—The various forms of a substance which show reversible transformations are said to be *enantiotropic*. Besides the enantiotropic forms, there may, also, exist monotropic forms. These latter are unstable at all temperatures (under the pressure concerned) but may nevertheless be formed and may persist indefinitely at ordinary temperatures. As the temperature is raised, the tendency to change to the stable form increases, until, finally, it may become so great that the monotropic form changes rapidly to the stable form. This temperature naturally constitutes an upper limit to the range of temperature at which the monotropic modifications can be formed. An important monotropic mineral is marcasite

¹ POSNJAK, ALLEN, and MERWIN, *Econ. Geol.*, Vol. X, pp. 491-535, 1915.

² *Op. cit.*, p. 526.

³ BATEMAN, "Geology of the Ore Deposits of Kennecott, Alaska," *Econ. Geol.*, Vol. XV, pp. 1-80, 1920.

⁴ BATEMAN, "Primary Chalcocite: Bristol Copper Mine, Connecticut," Vol. XVIII, pp. 122-166, 1923.

(FeS₂) which changes slowly to pyrite at 450°. ¹ Another monotropic mineral is aragonite (CaCO₃) which changes rapidly to calcite at 410°. Both these changes take place at appreciable rates at somewhat lower temperatures and, in the presence of a fluxing medium, will, no doubt, take place at considerably lower temperatures. ² The temperatures 450° for marcasite and 410° for aragonite may, therefore, be regarded as very considerably higher than those at which these minerals may be formed in nature.

Dissociation Temperatures.—The presence of a mineral containing a volatile constituent may sometimes be used as an indication of the temperature; but it must always be used with caution. The temperature of dissociation is very strongly affected by pressure in such cases, increasing pressure always raising the dissociation temperature. Thus, most zeolites can be formed only at a relatively low temperature, because they lose their water readily when heated, and if the geological relations are such as to indicate no great pressure, they can have formed only at decidedly low temperatures.

It will be noted that we are here using the fact of non-dissociation as an indication of absence of high temperature. The reverse process of using the apparent fact of dissociation to prove high temperature is fraught with much danger. Schneiderhöhn has considered the transformation of siderite into hematite as indicative of a temperature of at least 350 to 400°. He bases his reasoning largely on the fact that, when heated, siderite first shows appreciable change at about these temperatures. ³ It is very doubtful whether this reasoning can be regarded as valid unless the absence of solutions can be demonstrated. There are, unquestionably, solutions that could attack siderite and deposit hematite at much lower temperatures.

Dissociation and Reaction of CaCO₃.—The general failure of dissociation of CaCO₃ when it is heated in nature is not surprising, for, although CaCO₃ dissociates rapidly under atmospheric

¹ ALLEN, CRENSHAW, JOHNSTON, and LARSEN, *Am. Jour. Sci.*, Vol. XXXIII, pp. 187-188, 1912.

² Johnston, Merwin, and Williamson state that pure aragonite is transformed into calcite, when water and calcite are present, in the course of some days even at 100°. When isomorphous carbonates are present in solid solution in the aragonite, it is much more stable. *Am. Jour. Sci.*, Vol. XLI, pp. 473-512, 1916.

³ *Z. Kryst.*, Vol. LVIII, p. 326, 1923.

pressure at about 900°, it requires the weight of only 40 meters of rock to prevent dissociation at 1100°,¹ a temperature above which limestones have probably seldom been heated even at much greater depths.

When, however, another substance is present which can combine with CaO, the temperature at which CO₂ will be given off at a certain pressure may be much lower. Thus, CaCO₃ heated under a certain pressure in the presence of SiO₂ will begin to lose CO₂ at a lower temperature than will pure CaCO₃. We are here concerned with the equilibrium



the reaction taking place toward the right with rising temperature. If we were in full possession of the facts concerning this equilibrium, we could use them to determine temperatures of metamorphism of siliceous marbles. The presence of wollastonite (CaSiO₃) could not, in general, be safely used to indicate heating above a certain temperature, but coexistence of calcite and quartz would indicate failure of heating to that temperature, the pressure being assumed as known from other considerations.

V. M. Goldschmidt² has emphasized the importance of this equilibrium and has endeavored to calculate the *pt* curve, making use of the equation

$$\log p = \frac{Q}{4.571 T} + 1.75 \log T + C$$

in which *p* is the pressure of CO₂ corresponding to a temperature *T*, *Q* is the heat effect of the reaction, and *C* a constant of integration. The value of *Q* is but imperfectly known, and Nernst's assumption as to a definite value for the constant *C* has not proved altogether justifiable.³ No precise significance can be attached, therefore, to the values of the pressure and temperature calculated from the equation, and, as Goldschmidt himself notes, experimental investigation of the system is much to be desired. Goldschmidt has, thus, offered a very interesting attack on an important problem, but his calculated temperatures of 500 to 800° for pressure variation from 1 to 2,000 atmospheres

¹ From the data of SMYTH and ADAMS, *Jour. Am. Chem. Soc.*, Vol. XLV, p. 1178, 1923.

² GOLDSCHMIDT, V. M., "Die Gesetze der Gesteinsmetamorphose," *Vid. Selsk. Skr. I. Math. Naturw. Kl.* 22, 1912.

³ JOHNSTON, J., *Jour. Am. Chem. Soc.*, Vol. XXX, p. 1364, 1908.

as the limit of the stable coexistence of quartz and calcite cannot be regarded as accurate. There is, indeed, some indication that the temperatures corresponding to the various pressures should be somewhat lower.

Dissociation of Pyrite.—Pyrite dissociates on heating, with formation of pyrrhotite and sulphur vapor. The pressure of sulphur vapor in equilibrium with both pyrite and pyrrhotite at 615° is 20 millimeters. In other words, when the partial pressure of sulphur is 20 millimeters, pyrite cannot form above 615°, but iron sulphide must appear as pyrrhotite. At 675°, the pressure of sulphur at equilibrium with pyrite and pyrrhotite is 400 millimeters, and at 685° it is 1 atmosphere or 760 millimeters.¹ At higher temperatures, the pressures have not been determined, but the curve suggests that at 800° the pressure will have risen to some 40 atmospheres.

We have no satisfactory means of estimating the partial pressure of sulphur in mineralizing solutions and vapors. The highest sulphur content of volcanic gases from Hawaii analyzed by Shepherd was some eight volume per cent.² This corresponds with a partial pressure of sulphur of, roughly, 60 millimeters when the total pressure is 1 atmosphere. This vapor was, no doubt, released from solution in magma at a pressure at least a few times as great as the surface pressure, and if the partial pressure of sulphur can be assumed to increase in roughly corresponding ratio, we may deduce that natural solutions (magmas) can exist over which the partial pressure of sulphur vapor is at least a few times 60 millimeters. How many times we cannot say, but, if ten times, iron would be precipitated as the disulphide—pyrite—at all temperatures below 680° and as pyrrhotite above that temperature, provided, of course that a condition of saturation with iron sulphide were attained at these temperatures. It is, perhaps, possible that some sulphide deposits of the type known as *magmatic* are formed under conditions of temperature and sulphur pressure approaching those just noted.

Most mineralizing solutions become saturated with and, therefore, precipitate iron sulphide only at decidedly lower temperatures and under low partial pressures of sulphur. Under

¹ ALLEN and LOMBARD, *Am. Jour. Sci.*, Vol. XLIII, p. 192, 1917.

² SHEPHERD, E. S., *Bull. Hawaiian Volcano Observatory*, Vol. VII, p. 95, 1919.

such conditions, the most we can say is that pyrrhotite tends to indicate a higher temperature than pyrite. Pyrrhotite can, however, be formed from the right kind of solution at very low temperatures.

INFORMATION AFFORDED BY INCLUSIONS IN CRYSTALS

Besides changes of state of aggregation such as those involved in inversion or melting, any property which changes with temperature may be used to determine the temperature of formation of a mineral if some record of the change is left. The classical researches of Sorby¹ on the fluid inclusions in the cavities of crystals furnish an excellent example. Here the temperature of formation of the crystal is deduced from the amount of contraction of the liquid, on the assumption that the liquid formerly filled the cavity and that the relative contraction is given by the relative volume of the bubble and that of the entire cavity. In general, the greater the relative size of the bubble the higher the temperature at which the liquid was enclosed. For the accurate solution of this problem, it would be necessary to have a complete knowledge of the thermodynamic properties of the substance occurring in the cavity. For no substance is such knowledge available. Regarding the substances ordinarily occurring in the cavities, namely, water, aqueous solutions, and liquid CO₂, enough is known to enable us to reach some general conclusions. At temperatures up to, perhaps, 300° the compressibility of water is sufficiently small so that lack of knowledge of the pressure does not introduce great uncertainty into the volume of the liquid as fixed by temperature alone. As the critical temperature is approached, however, water becomes much more highly compressible, so that the pressure is as important as the temperature in determining the volume. Above the critical temperature, the pressure is, of course, exceedingly important in its effect upon volume. It is possible, for example, that at a temperature somewhat above the critical temperature, a cavity might be filled with gaseous H₂O under a pressure several times the critical pressure. Such a cavity might be almost entirely, or, indeed, entirely, filled with liquid water when cooled to room temperature. One might be led to conclude that the crystal was formed at a temperature only a little above room temperature,

¹ SORBY, H. C., *Quart. Jour. Geol. Soc.*, Vol. XIV, pp. 453-500, 1858.

whereas it was actually formed above the critical temperature of water.

In fact, if the cavity was filled by a gas above its critical temperature, the problem becomes insoluble. In the case of cavities containing liquid CO_2 , for which this condition is, of course, always true, it has been suggested that the relative volume of liquid and bubble can be used to estimate the temperature at which the crystal was formed if the pressure is assumed known. In other words, a curve of variation of temperature with pressure can be constructed for each ratio of the volume of the bubble: the volume of the cavity.¹ The construction of such a curve is, however, based not on any ascertained data for the gas but upon calculation with the aid of one of the equations of state, say Van der Waal's or Dieterici's; and modern research shows very convincingly that these equations deviate widely from the facts, even under the rather limited range of conditions which have been investigated. It is doubtful, therefore, whether any useful information is to be gained from considerations based on these equations.

In spite of these numerous limitations, it is no doubt true that the fundamental assumption ordinarily made is frequently justified; that is, that the cavity was filled with liquid and the volume of the liquid was sufficiently independent of the pressure so that the amount of cooling can be determined from the decrease of volume.² In many cases, other evidence can be brought to bear on the problem, and frequently it confirms the low temperature estimated as the temperature of formation on the basis of the liquid inclusions. It is unquestionable, however, that many of the estimates of the temperatures of crystallization of granite quartzes, as obtained by Sorby, are altogether too low. In some cases, this may be due to the fact that the quartz was recrystallized at low temperatures, but in others, it is probably to be referred to the limitations of the method, which tend to give a low value, as shown by the considerations brought out in the foregoing discussion.

¹ JOHNSEN, A., *Sitzb. Bayer. Akad. Wiss., Math.-physikal.-Kl.*, pp. 321-328.

² Some investigators have not placed reliance upon calculation of change of volume but have resorted to direct observation of the temperature of disappearance of the bubble upon heating the crystal. HOLDEN, *Am. Mineral.*, Vol. X, p. 218, 1925.

When the liquid is a solution, as it frequently is, and especially when it is a strong solution, the critical temperature of water would, of course, be raised; indeed, critical phenomena might be excluded altogether. In such a case, the ordinary consideration of expansion of a liquid could be extended to somewhat higher temperatures, but the solutions would have such high compressibility at these temperatures that a low estimate of the temperature of formation of the crystal might well be reached if the temperature had been very high and the pressure, also, very high.

The fact that smoky quartz and amethyst lose their color upon heating has been regarded as indicating that these minerals must have formed at temperatures below those at which the color disappears. The minimum temperatures of decoloration have been established by Holden at 240 to 260°. ¹ But since Holden has shown that colorless quartz may become smoky by exposure to radium emanation and that heat-decolorized quartz of both varieties may have its color restored by irradiation, it is doubtful whether the presence of these colors in quartz can be uniformly regarded as indicating a lack of exposure to high temperatures at all stages in the career of the crystal. Perhaps, in some instances, the zonal distribution of color may suggest that it was the radioactivity of the depositing solution which caused the smoky character and, thus, indicate a low temperature of formation. A quartz crystal with minute, zonally distributed, radioactive inclusions might, however, acquire zonal coloring at low temperatures even though formed at high temperatures, so that the zonal condition must be used with caution. Nevertheless, it does appear to be true that smoky quartz occurs where there is evidence from other sources of a low temperature of formation.

Deposition of Salts from the Included Solution.—In some cases, the liquid of these inclusions has deposited some of its dissolved salts on cooling. Lindgren and Whitehead have used the relative proportion of deposited salt to saturated solution in order to estimate the temperature of formation of the enclosing quartz crystal. ² Because the crystals are cubes, they conclude that they are halite (NaCl). By extrapolation of the solubility curve of sodium chloride, on the assumption that it is continuous

¹ HOLDEN, *Am. Mineral.*, Vol. X, pp. 203-252, 1925.

² LINDGREN, W., and W. L. WHITEHEAD, *Econ. Geol.*, Vol. IX, p. 455, 1914.

to the melting point of NaCl, they concluded that the temperature would have to be raised somewhat above 500°, in order that all the salt might be just taken into solution, and that the temperature 500°, therefore, constitutes a minimum temperature of enclosure of the salt solution. It is a minimum temperature because one cannot safely regard the solution as exactly saturated.

The assumption that the solubility curve is continuous to the melting point, while justifiable for many salts, is not altogether safe for NaCl. This salt is of rather sparing solubility, and its solubility increases but slowly with temperature. At 210°, the highest determined point, it already shows signs of a decreasing temperature coefficient of solubility which may presage critical phenomena. The indications are, then, that the solubility curve of NaCl is not continuous but consists of two portions separated by a critical region. The 53.6 per cent solution, which would be obtained were all the salt crystals in solution,¹ may be incapable of existence except above a second critical end-point, under temperature and pressure conditions which there is no means of estimating. If, however, the condition assumed by Lindgren and Whitehead really obtains, and if we estimate the temperature by their method, using the corrected value for the strength of the solution and, also, the correct melting point of NaCl, 801°, we obtain a value about the same as theirs, *viz.*, an indicated minimum temperature somewhat above 500°. Nevertheless, it would appear that a more reasonable assumption as to the nature of the cubic crystals is that they are sylvite (KCl). This salt has a high temperature-coefficient of solubility. At 180°, the solution already contains 44 per cent, and the solubility is increasing so rapidly at this point that almost certainly no critical phenomena ensue; indeed, the melting point of KCl lies on a rational extrapolation of the solubility curve as determined up to 180°. The extrapolated curve indicates that a solution containing 53.6 per cent KCl² could exist at 280°. The minimum

¹ Lindgren and Whitehead calculated that this solution would be 57.5 per cent salt. They either made some slip in calculation or used an incorrect figure for the strength of solution at 20°C.

² Probably the measurement of the volume of the crystals relative to solution is not sufficiently accurate that this figure need be corrected for the lower density of KCl. Moreover, KCl has nearly the same solubility as NaCl at room temperature, so that no modification of the calculation is required on that score.

temperature of enclosure of the solution as thus obtained is 280° or, say, about 300° .

Each of these estimates is based on the assumption that the liquid is a pure solution of the individual salt considered. As a matter of fact, it is more likely to be a solution of both chlorides with, perhaps, other salts. If the other salts are present in such quantity as to exert a negligible influence on the solubilities of the chlorides, then the actual temperature estimates given above need not be significantly changed; that is, a temperature of at least 500° if the cubes are NaCl and of at least 300° if the cubes are KCl would still hold approximately, even if both chlorides were present in the solution. This fact is indicated by the approximate parallelism of the saturation isotherms of NaCl and, also, of KCl in the ternary system H_2O -NaCl-KCl, which are, however, known only to 100° .¹ If the cubes are both KCl and NaCl, the conditions are more complicated, and the problem is insoluble unless their relative proportions are known. It is to be noted, however, that, if both are present, the last effects of cooling, so far as NaCl is concerned, should be a resolution, and it might be expected that this would be recognizable in a rounding of the NaCl crystals, whereas the KCl would be in sharp cubes.

Lindgren and Whitehead prefer to regard the cubes as NaCl on account of the presence of albite, but there is nothing in this fact to preclude the possibility that they are KCl.

It is plain that no very definite solution of the problem is to be reached on the basis of the proportion of these crystals. We have, however, an alternative to the solution given by Lindgren and Whitehead, which is at least as definite as theirs. Let us examine these two alternatives. The temperature was above 500° , if we assume the crystals are NaCl, indeed, probably considerably above, if, as seems likely, critical phenomena intervene in NaCl solutions. The temperature was, perhaps, not more than 300° if we assume the crystals are KCl. We are led to wonder whether there is not some feature of the deposit that may enable us to decide between these two temperatures. As a matter of fact, there is; this feature is the presence of jamesonite ($2PbS \cdot Sb_2S_3$). This mineral melts at $609^{\circ}C$. It melts incongruently, breaking up into liquid and PbS ,² but, for our present

¹ BLASDALE, *Jour. Ind. Eng. Chem.*, Vol. X, p. 348, 1918.

² JAEGER and VAN KLOOSTER, *Z. anorg. Chem.*, Vol. LXXVIII, p. 262, 1912.

purpose, this is just as useful as congruent melting, for it puts just as definite an upper limit to the existence of jamesonite. The jamesonite of the deposit under discussion was formed in the presence of arsenopyrite, pyrrhotite, and zincblende, and there can be no question that the liquid formed when jamesonite melts can take a considerable quantity of such sulphides into solution. In other words, the temperature of (incongruent) melting of jamesonite would be lower in the presence of these substances and probably very much lower. It is very doubtful, therefore, whether jamesonite could be deposited above 500° in the presence of these minerals even from a dry melt. Since it was actually deposited from complex aqueous solutions, there can be no question as to the choice between 500 and 300°, at least for the formation of the jamesonite. While recognizing a definite sequence of minerals, with quartz among the earliest and jamesonite among the latest, Lindgren and Whitehead were sufficiently convinced of their approximate contemporaneity to be willing to fix the temperature of formation of the jamesonite by that of the formation of quartz. If they were justified in doing so, the reverse process is equally permissible, and we may fix the temperature of formation of the quartz as probably not much above 300°. We have, thus, additional reasons for preferring the temperature obtained, on the assumption that the cubic crystals in the quartz cavities are KCl. Jamesonite is regarded by Lindgren as ordinarily indicative of intermediate temperatures. It is more than probable that this jamesonite deposit is altogether normal in its temperature relations and not of exceptionally high temperature, as Lindgren and Whitehead conclude.

GENERAL CONCLUSIONS

From the general trend of the discussion of the facts used to determine temperatures of geologic processes, it will be plain that there is, ordinarily, much room for the exercise of judgment and for the balancing of probabilities. Only rarely can a rather definite temperature of formation be assigned to a certain mineral sample without considering it as merely one phase in a sequence of mineral deposition. Some few reference points are known with considerable accuracy, and to these must be tied a train of events with the aid of observed geologic relations and mineral paragenesis.

The principal points of reference are:

1. Actual measured temperatures of lavas and, to some extent, of fumaroles and springs.

2. Melting points, particularly low melting points, for minerals of a certain class as indicating maximum possible temperatures, such as albite 1100°, stibnite 546°, bismuth 271°.

3. Inversion points, as indicative of both maximum and minimum temperatures, such as wollastonite \rightarrow pseudowollastonite 1180°; quartz \rightarrow tridymite 870°; α - β -quartz 573°; chalcocite 91°.

In addition to these more general points, it is sometimes possible to get reference points for individual cases on the basis of the amount of contraction of fluid inclusions in cavities of crystals and the deposition of salts from the solution in the cavities.

Again, there are the general indications of low temperature afforded by the presence of monotropic substances, such as marcasite and aragonite, and the presence of substances easily decomposed by heating, such as the zeolites.

The following brief summary may be given of the conclusions which have been reached regarding temperatures of mineral formation in various types of rocks and ore bodies. Deductions may be based on minerals present in the immediate wall rock of a deposit as well as on those of the deposit itself.

TEMPERATURES OF FORMATION OF MINERAL MASSES

Igneous Rocks.—In part, above 870° for the earliest minerals of the more basic rocks. Principally, between 870 and 600° and, in a general way, decreasing with increasing silica content.

Indicators: Direct measurements of temperatures of lavas. Low melting temperatures of alkaline feldspars even in dry melts. Presence of inverted quartz.

Mineral Deposits Formed by Simple Local Accumulation in Magmas Exclusive of Residuary Segregations Involving High Concentration of Volatiles.—Temperatures corresponding with those above and varying with the nature of the deposit and the associated rocks.

Indicators: Presence of the ordinary igneous-rock minerals as syngenetic constituents of the deposit.

Regional Metamorphic Rocks.—Widely varying temperatures up to and perhaps occasionally including temperatures of refusion.

Indicators: Nature of the quartz. Presence of pyroxene or hornblende or chlorite. Many others impossible to discuss in small compass.

Mineral Bodies Formed by Thermal Contact Metamorphism.—Very rarely and locally upward of 1200° ; occasionally, and in restricted amount, somewhat above 870° , but generally below 870° .

Indicators: Rare local melting of wall rock, occasional transformation of quartz to tridymite or cristobalite but common failure of transformation of quartz. Recrystallization into mineral species analogous to those of igneous rocks, *e.g.*, pyroxenes.

Mineral Masses Formed by Metasomatic Contact Metamorphism.—Transitional into those of thermal metamorphism and, occasionally, above 573° . Usually below that temperature and graduating into replacement deposits of relatively low temperature.

Indicators: Paragenetic relationship to deposits formed by thermal metamorphism. Presence of minerals analogous to basic igneous-rock minerals in those formed at highest temperatures. Presence of the high-temperature sulphide pyrrhotite in those of higher temperature. Nature of the quartz.

Pegmatites and Residuary Segregations Involving High Concentration of Volatiles.—Granite pegmatites in the neighborhood of 573° . Other deposits, such as some magnetite masses, not well understood but suggesting analogous conditions.

Indicators: Both inverted and uninverted quartz.

Veins and Replacements.—Temperatures below 573° and graduating down to those but little above the ordinary temperature.

Indicators: Paragenetic relationship to pegmatites and contact metamorphic deposits. Presence of uninverted quartz. High-temperature sulphide groupings emphasizing iron and copper in those of higher temperature. Sulphides of antimony and arsenic and complex sulphosalts in those of lower temperature. Fluid inclusions in crystals. Nature of wall-rock minerals, such as hornblende for higher temperatures, chlorite for lower.

CHAPTER XI

THE ENRICHMENT OF SILVER ORES

BY F. N. GUILD

INTRODUCTION

It so happens that the earth is made up essentially of a very few elements. Many of the economically valuable metals, as silver, copper, nickel, and gold, are, from the broader geologic standpoint, of insignificant importance. They are present in the primary rock in such small quantities that even the specific mineral in which they occur is usually unknown. It can only be surmised that they are present here either as disseminated particles, isomorphous mixtures in some of the rock-forming silicates, or in the state of solid solution in the primary and accessory minerals. In all of these cases, they may be invisible even under high magnification, for even when present in disseminated particles they may be in submicroscopic grains. That these metals are there in the primary rock, however, has repeatedly been shown by careful chemical analysis. Yet in order to form an economically valuable deposit, in order, in fact, to develop a deposit in which the specific minerals of these elements may be microscopically recognized, an intricate process of concentration or enrichment must have taken place. It is not the purpose of this paper to discuss in detail all of these processes. In fact, many of the earlier ones are still so lacking in satisfactory data that very little can be done even in the construction of good working hypotheses. The procedure may, however, be briefly outlined as follows:

1. Magmatic Concentration.—Certain acid or basic differentiation products of the primary rock may be richer in the valuable ore metals than the parent mass. In few cases only, as, for example, with chromium, does this process alone give rise to sufficient concentration to yield a workable ore deposit.

2. Hydrothermal Concentration.—A further process of concentration now sometimes takes place in these magmatic

differentiates. This we believe to have been accomplished by percolating solvents either pneumatolytic or hydrothermal. These have migrated through the differentiate, having escaped, most probably, from the parent mass or from some other associated igneous body. These solutions, as they penetrate farther and farther from their source, suffer a diminution of pressure and fall of temperature or else come in contact with precipitating agents, as a result of which early ore and gangue minerals are left behind in the form of disseminated particles, veins, or other type of deposit.

3. Hypogene Enrichment.—As these solutions proceed along certain channels predetermined by geologic agencies, a process of further concentration takes place by which the early and less valuable minerals are replaced and cavities filled, and, thus, the lead, copper, or silver minerals begin to make their appearance in greater abundance. This may be termed *upward, primary, or better, hypogene enrichment*.

4. Supergene Enrichment.—Finally, after the hypogene solutions have accomplished what they can in the deposition of the primary or earlier ore minerals, surface solvents percolating downward and bearing oxidizing gases may bring about a further deposition of minerals frequently still richer in the desired ore metal. This is *supergene replacement* or what is commonly known as *secondary or downward enrichment*. These enrichment products may be found in the oxidized zone in the form of insoluble salts, as silver chloride, or in the zone immediately below in the form of sulphides or sulphosalt minerals.

The above is but a very brief outline illustrating the main features by which many ores are concentrated or enriched by geologic and mineralogic agencies from the lean country rock. Silver is no exception to the rule. It is probably present in all rocks and sea water, though the published reports as to the exact quantities are somewhat conflicting. In many rocks, it seems to exceed 1 gram of silver per metric ton.¹ As in the case of copper enrichment, the process of replacement may start with a mineral containing none of the essential metal. In fact, although the process of replacement, or the succession of deposition, is usually spoken of as beginning with the lean or early sulphide, it should be borne in mind that these, too, have

¹ For the results of various workers, see LINDGREN, "Mineral Deposits," p. 10, 1919.

taken part in still earlier processes, since they have replaced, or followed, quartz, or other non-metalliferous mineral of the vein. Even the gangue minerals, many of which must have been concerned with reactions with the rock-forming silicates, have crowded themselves in by virtue of replacements in the wall rock or brecciated material. Thus, starting with the primary constituents of the rock, a complete succession of minerals might be traced, ending up, in some cases, with the native metal.

It is the purpose of this investigation to trace some of these replacement processes in silver-ore deposition as revealed by the reflecting microscope.

RELATIONS OF THE SILICATES, GANGUE MINERALS, AND ORES

Comparatively little has been done in the accurate microscopic study of the relationship of the gangue minerals to the silicates or their alteration products. What work has been accomplished has been more or less incidental to other lines of research and, therefore, lacks the detailed data which might come from a specific investigation. The fact that vein quartz may replace the silicates of the wall rock is familiar to all. This may take place in such a manner that the structure of a porphyritic rhyolite or brecciated andesite may be quite thoroughly preserved, although the mass now contains little or even none of the original silicates. Replacements of the silicates by calcite, sericite, and other silicate minerals are of frequent occurrence, as observed in the study of thin sections. The relation of fluorite, barite, and less common gangue minerals could well be made the subject of a specific study. The reflecting microscope frequently brings out these relationships, even for the non-opaque minerals, to better advantage than the polarizing instruments. Thus, in Fig. 1, a tracing from a photograph of a polished surface of vein material from Sandon, British Columbia, calcite is seen replacing quartz, leaving residual grains with irregular outline. This at once calls to mind a typical structure often observed among the ore minerals. The same specimen when viewed as a thin section merely shows a crystalline aggregate of transparent minerals, the relationship of which is difficult to make out. The cause of these replacements is to be sought in the fact that geologic changes have brought about new conditions

unfavorable to a continuation of the state of equilibrium of the earlier-formed minerals.

The phenomena of replacement of the silicates directly by ore minerals, especially with reference to high temperature and magmatic deposits, have recently received considerable attention. Thus, the early work of Berg¹ emphasized many cases of



FIG. 1.—Calcite replacing quartz, Sandon, British Columbia. This illustrates how gangue minerals may show the same replacement structures as ores. Quartz (lined) remains as residual grains. The same specimen, when viewed as a thin section under polarized light, appears as a cryptocrystalline mass of quartz and calcite, the correct relationship of which is not apparent. $\times 370$.

rock-forming and contact silicates replaced by ore minerals. He showed pyrrhotite crossing diallage and plagioclase in a system of fine veinlets, chalcopyrite zonally replacing garnet, and sphalerite replacing anthrophyllite. Later, Tolman and Rogers² made an exhaustive study of the relation of many of the

¹ BERG, "Mikroskopische Untersuchung der Erzlagernstätten," Berlin, 1914.

² TOLMAN and ROGERS, "A Study of the Magmatic Sulfid Ores," *Stanford Univ. Pub.*, 1916.

ore minerals to the silicates. Lindgren¹ states that pyrite and galena may replace feldspar and calcite, and Fenner² found the ordinary constituents of a rhyolite replaced by stephanite and chalcopyrite. This is similar to Fig. 2, illustrating a polished specimen from Sandon, British Columbia, where we have a brecciated condition in quartz and other material, in which the

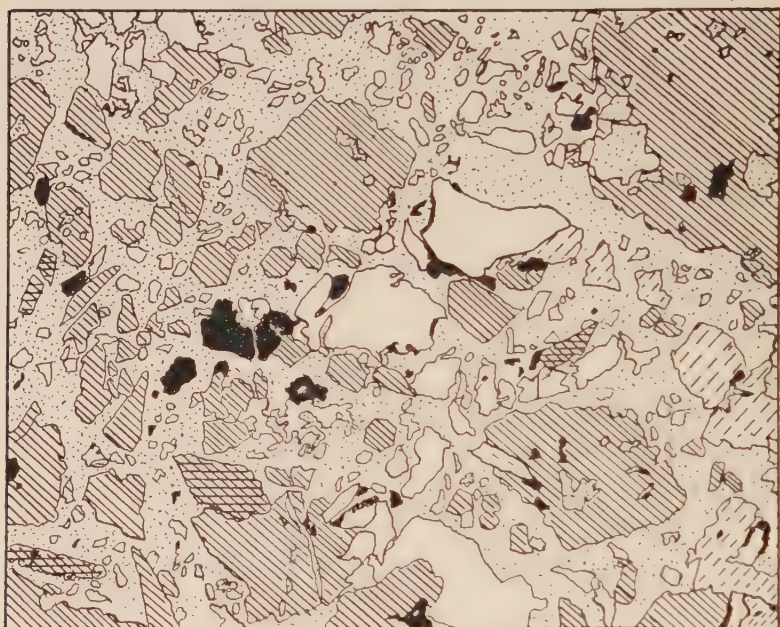


FIG. 2.—Brecciated gangue material replaced by stephanite, pyrite and sphalerite. Sandon, British Columbia. This is an example of a silver mineral and other sulphides replacing silica or a silicate gangue. Stephanite, white. Pyrite, broken lined. Sphalerite, cross-lined. Quartz, lined. Calcite (mainly), dotted. Hole, black. $\times 25$.

fragments have clearly been replaced by pyrite, sphalerite, and the silver mineral stephanite. Argentiferous galena replacing calcite in cleavage directions, or, perhaps, forming in capillary cracks and later enlarging them by force of crystallization, is represented in Fig. 3, illustrating a polished specimen from Broken Hill, Australia. Other portions of the same section show galena replacing the calcite in jagged outlines.

¹ LINDGREN, "Mineral Deposits," 1919, p. 26.

² FENNER, "A Replacement of Rhyolite Porphyry by Stephanite and Chalcopyrite at Leadville," *School Mines Quart.*, Vol. XXXI, p. 235, 1909.

In the laboratory, Sullivan¹ found silver to be precipitated by many silicates, as orthoclase, albite, clay gouge, amphibole, and others. Van der Veen² has emphasized the action of colloids, such, perhaps, as clay gouge, as possible precipitants of native metals, as copper, gold, and silver in the following words:



FIG. 3.—Argentiferous galena (dotted) replacing calcite (white) along crystallographic directions, or perhaps merely filling and enlarging cleavage cracks. Broken Hill, Australia. Large masses of galena in the same specimen show undoubted replacement with residual grains of calcite in the galena. $\times 100$.

Probably the occurrence of extremely fine gold in kaolin is also due to the adsorption power of the colloidal kaolin material on gold solutions, which drop their gold ions when their electric charges are neutralized by the negatively charged kaolin.

Attention is also called to the inability of the positive colloid, ferric hydroxide, to accomplish this result, except when mixed with the negative manganese-oxide colloid.

¹ SULLIVAN, *U. S. Geol. Sur. Bull.* 312, 1907.

² VEEN, VAN DER, "Mineragraphy and Ore-deposition," p. 108, The Hague, 1925.

SUCCESION OF DEPOSITION AND REPLACEMENT PROCESSES OF THE EARLY SULPHIDES

The microscopic study of ore deposits has emphasized the fact that the most prominent ore minerals form sequences of deposition which do not vary much from one ore body to another. Starting with the higher-temperature vein minerals, the sequence has been worked out somewhat as follows:

Hypogene	Supergene
Arsenopyrite	Chalcopyrite
Pyrite	Bornite
Sphalerite	Chalcocite, with stromeyerite
Chalcopyrite	Argentite and sulpho-salt minerals
Tetrahedrite	of silver
Chalcopyrite	Covellite
Bornite-chalcocite intergrowths	Native silver
Galena (sometimes with argentite spots)	Oxidized ore minerals,
Sulpho-salt minerals of silver	malachite, azurite, cerussite,
Native silver, formed on the early sulphides	anglesite, cerargyrite

The investigation of the role played by the rich silver minerals with reference to the members of these series is the main object of this chapter and will, therefore, not be summarized until later. We may say here, however, that they may replace almost any of the earlier ore minerals and that a really definite position in the above scheme can hardly be given with the data at present available. The fact should be emphasized, nevertheless, that data in regard to silver ore deposition have to be obtained largely from a study of associations with the better-known and more abundant copper and lead minerals. Chalcopyrite appears to occur principally in two rather distinct generations, one earlier—perhaps itself divided into two subgroups—and the other distinctly later than galena. The earlier type may be definitely replaced by galena, as it shows ragged residual grains, while the later type is confined mainly to smooth filling along the cleavage cracks of galena. It seems rational to place the earlier types as hypogene and the later as supergene.

The question of hypogene and supergene chalcocite is a matter of considerable importance in the paragenesis of some of the silver minerals, but, further than placing the bornite-chalcocite intergrowths as hypogene, the subject will not be enlarged upon.

Arsenopyrite.—As is well known, this mineral is frequently associated with silver ores together with pyrite, galena, and sphalerite. When so associated, we have invariably found it to be the oldest ore mineral present. Yet Newhouse¹ refers to certain Mexican deposits where pyrite is “closely followed by arsenopyrite.” Our observation corresponds more with the

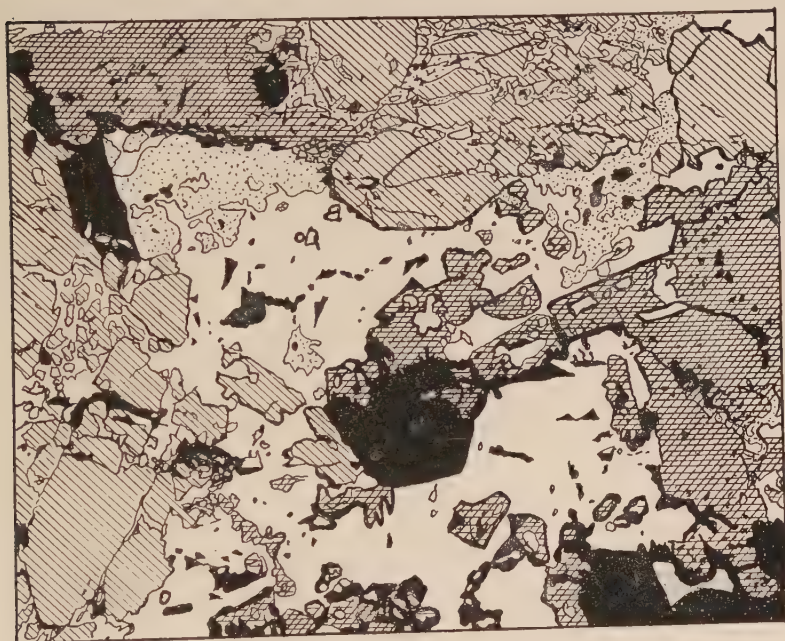


FIG. 4.—Arsenopyrite with later pyrite, galena, and ruby silver. Mexico. Arsenopyrite, lined. Pyrite, cross-lined. Galena, white. Proustite, dotted. Holes, black. Pyrite is later than the brecciated arsenopyrite as shown by its mechanical relation to the fracturing, a fact not well brought out by the drawing as a larger area is required. Pyrite shows a tendency to skeleton structure, the negative crystal-like cavities being filled with galena. Galena and proustite are later than the two other sulphides. $\times 81$.

general opinion that it is a high-temperature mineral, as its occurrence in veins of pegmatitic affinities would indicate. When associated with pyrite, arsenopyrite is often shown to be earlier, not by the evidence of a direct process of replacement or corrosion but by a consideration of the fracturing. Thus, in Fig. 4 may be seen rather definite crystals of arsenopyrite

¹ NEWHOUSE, “Paragenesis of Marcasite,” *Econ. Geol.*, Vol. XX, p. 54, 1925.

greatly fractured, with pyrite and argentiferous galena filling the spaces between. Arsenopyrite does not seem to be corroded by pyrite, but both are replaced by galena, pyrite probably more easily than arsenopyrite.

Galena in this specimen is further associated with proussite, the arsenical ruby silver, which is apparently later. It appears in irregular masses and sometimes extends along borders between galena and pyrite. This last feature is the only evidence in this particular specimen of its later origin. There is, also, no criterion here that might lead one to an opinion as to whether the late silver mineral is hypogene or supergene. Ruby silver replacing galena in structures which cannot be mistaken will be described later, and this may, perhaps, be looked upon as a different era of deposition from the one just described. The first may be hypogene and the later, supergene. However that may be, we have here an example of progressive enrichment, as the first mineral, arsenopyrite—not to mention the still earlier gangue minerals—probably contained but traces of silver, the galena a much larger amount, and, finally, the proussite becomes the richest of all. A further enrichment to native silver may be observed in some specimens. Proussite has been seen to extend into arsenopyrite in veinlets, and it may, therefore, be inferred that the silver solutions have been fixed by reaction with the sulphoarsenic compound.

Pyrite.—Pyrite is a more characteristic vein mineral than arsenopyrite, and though it ranks second in the series given above, in the more typical veins it is the first ore mineral to take part in replacement processes. In the paragenesis of the silver minerals, this seemingly unimportant sulphide should not be neglected. Investigations seem to show that it plays an important role in the later enrichment of the silver ores. This is probably concerned with oxidation processes and is, therefore, supergene. Thus, from geologic considerations, Weed,¹ has observed that enrichment has not taken place in the absence of this sulphide, although other conditions were favorable. With pyrite present, abundant rich silver minerals have made their appearance. Furthermore, laboratory experiments have confirmed the opinion that iron sulphate as well as a certain concentration of hydrogen ions assist in the solution and transportation of silver and other

¹ WEED, "The Enrichment of Gold and Silver Veins," *Trans. Am. Inst. Mining Eng.*, Vol. XXX, p. 439, 1900.

metals. These conditions are obtained by oxidation of pyrite and hydrolysis of the sulphate of iron. The results of these laboratory experiments, of course, help to explain supergene enrichment. Frequently, however, rich silver minerals have made their appearance in the presence of pyrite where the evidences of supergene action are wanting, and yet a certain kind of enrichment has taken place apparently independently of the sulphide.

Pyrite as a supergene mineral has been mentioned from time to time. Allen¹ has found iron disulphide as pyrite and marcasite to be deposited from cold laboratory solutions of low acidity containing ferrous sulphate, sulphur, and hydrogen sulphide. Pyrite as pseudomorphs after argentite and polybasite has also been observed in nature. These are generally looked upon as supergene, though the deposition of later pyrite may, in some cases, be due to the reopening of channels of fresh hypogene solutions. In the study of a series of copper-silver ore specimens from Cerro de Pasco, Peru, pyrite was found in some samples to be apparently earlier than the enargite-famatinite intergrowths and in others later. In this investigation, attention was called to the fact that either enargite-famatinite could be considered the constant mineral with two generations of pyrite or pyrite could be taken as such, in which case, the enargite-famatinite would be appearing in two generations, one earlier and the other later than pyrite.

Many of the silver deposits contain sufficient copper to show all of the alterations of pyrite so often observed in the rich copper veins. Thus, it is found altering to chalcopyrite, then to bornite, and, finally, to chalcocite and covellite. The Silver King Mine, of Arizona, being particularly rich in copper minerals, shows this feature to a remarkable degree. Here all the features of copper enrichment are observed parallel with a progressive enrichment of the silver, probably both hypogene and supergene.

Sphalerite.—This mineral, being also a frequent associate of silver ores, should not be omitted in the investigation. It is not found actively replacing pyrite, *i.e.*, in the form of veinlets and other characteristic replacement structures; and the evidence of its later deposition lies in the fact that it most frequently occurs as a more or less complete filling in the spaces formed by

¹ ALLEN, "Sulphides of Iron and Their Genesis," *Mining Sci. Press*, Vol. CIII, p. 414, 1911.

the brecciation of the pyrite. At Leadville, Colorado, Blow¹ has described it as being dissolved in the oxidized zone and redeposited below. Emmons,² however, is not of the opinion that sphalerite "is precipitated by secondary processes along with copper, silver and gold." In this investigation, it has not been observed as a late mineral, its most characteristic place being just after pyrite. Sphalerite has sometimes been observed in association with the late sulphides in what appear to be residual veinlets. On superficial observation, these seem to be later than the associated sulphides. An example of this sort has been observed from the Harcuvar Mountains, in Arizona. The material appears under low power (hand lens) as sphalerite veinlets, frequently branching and crossing each other in an area consisting mainly of chalcopyrite and chalcocite. On observation with higher magnification, the sphalerite is found to be crossed by an extremely complex network of chalcocite veinlets. Furthermore, all the grains of sphalerite are bordered with thin coatings of chalcocite. These are characteristic replacement structures. It is thought that the sphalerite first formed in veins in some gangue material, the gangue minerals being later replaced by the late copper ores. Of these, chalcocite has been especially active in replacing the sphalerite, also.

Frequently, rich silver minerals, as the ruby silvers, are found extending into sphalerite in the form of crack fillings and incipient veins. These relationships seem to be more or less incidental features connected with the more pronounced replacement by these minerals of the associated tetrahedrite and galena. Sphalerite is very frequently filled with spots and laths of chalcopyrite often crystallographically arranged. These are thought to represent unmixing or segregation from a homogeneous state. An argentiferous antimony mineral, probably related to jamesonite, has been observed in somewhat similar relationships in the sphalerite of the Precious Metal Mine, Silver City, Idaho. The silver mineral also occurs here in larger masses apart from sphalerite, evidently replacing milky quartz.

Tetrahedrite.—The data regarding the position of this mineral in the series seem to be somewhat conflicting. It should be

¹ BLOW, "Geology and Ore Deposits of Iron Hill, Leadville, Colo.," *Trans. Am. Inst. Mining Eng.*, Vol. XVIII, p. 169, 1890.

² EMMONS, "The Enrichment of Ore Deposits," *U. S. Geol. Sur. Bull.*, 625, p. 381, 1917.

remembered, however, that the earlier results were secured without the use of the reflecting microscope and, therefore, in many respects may be unreliable. When argentiferous (freibergite), this mineral becomes of great importance as a source of silver and, therefore, in our present work will be considered in some detail. There is no evidence that freibergite is an enrichment product of non-argentiferous tetrahedrite. The portion made up of the complex silver molecule is not visible under the microscope, the surface appearing perfectly smooth and homogeneous. It is, therefore, present as an isomorphous mixture with the copper molecule. Furthermore, it is not believed to be a later addition either hypogene or supergene. This condition should, however, be clearly distinguished from those cases described later where silver minerals, as stromeyerite or ruby silver, are found in veinlets, cavity fillings, and spots in, perhaps, only slightly argentiferous tetrahedrite. This seems to represent a breakdown of tetrahedrite by which the material becomes enriched by these later additions, many of which may have been derived from leaner areas.

Tetrahedrite as an early mineral has been mentioned from the Cripple Creek district, where it persists to a depth of 2,000 feet. In Butte, Montana, it is also described as an early mineral, though the corresponding arsenic compound was thought to be later. On the other hand, it has been described as secondary at Bingham, Utah, and Rio Tinto, Spain. It is still more emphatically described as a late mineral in the Georgetown Quadrangle, Colorado, where it is stated to be the "last of the silver minerals to form." In the paragenesis of minerals, geologic data are of great importance, and it has usually proved true that they are in remarkable harmony with the more recent microscopic data. In this case, however, it is our opinion that tetrahedrite is normally an early hypogene mineral finding its place between sphalerite and galena. As with many of the early sulphides, the replacement structures or other evidences of sequence are not so clear here as could be desired. The evidence lies in the rather obscure veinlet structure, not often observed, as well as a marked tendency to find residual grains of sphalerite in tetrahedrite areas, whereas such grains of tetrahedrite are not often observed in sphalerite. If these conclusions are true, then tetrahedrite becomes the earliest recognizable source of many of the later and richer silver minerals. Thus, in

Fig. 9, described later, it is replaced by the rich silver mineral, stromeyerite, and it is frequently seen to have spots and veinlets of ruby silver.

That tetrahedrite is a more prolific source of silver in the later deposition of rich silver minerals than is galena, has further been shown by analyses made from material secured from the surfaces of polished specimens. From 50 to 100 milligrams of the material were obtained from the different areas by means of a sharp awl. The tetrahedrite even under high power was seen to be perfectly homogeneous, showing the silver content to be isomorphously mixed. The galena areas were not quite homogeneous but showed numerous small spots. In a specimen from the Nettie L. Mine, Ferguson, British Columbia, tetrahedrite grains were found to contain 7.27 per cent silver, while the galena grains contained only 0.23 per cent. A similar specimen from the Silver King Mine, Arizona, showed, for the tetrahedrite grains, 6.06 per cent silver, while the galena grains contained 1.24 per cent. In this case, the galena contained numerous inclusions too small to be discarded. These were thought to be residual tetrahedrite, as in other portions of the section the evidence was strong that the galena had definitely replaced the tetrahedrite. Other specimens showing areas of tetrahedrite with spots and veinlets of ruby silver (proustite) have been enriched either by hypogene or supergene solutions. Such grains were found to contain as high as 25.02 per cent silver.

Galena.—Galena has been found in silver veins showing conclusive replacement structures with reference to arsenopyrite, pyrite, and sphalerite. In all of these cases, definite veinlets and corroded borders have been observed. Its relation to tetrahedrite is not quite so self-evident, however; it is firmly thought to be later. The characteristic structure is that of residual grains of tetrahedrite in the galena and very ragged or corroded borders. These borders show many more reentering tongues of galena into tetrahedrite than tetrahedrite into galena. Also, near the borders between the two there appear many more apparently residual grains of tetrahedrite in the galena areas than corresponding grains of galena in the tetrahedrite areas. There are, however, many specimens which show stretches in galena, of tetrahedrite which, under the hand lens, appear to be later. Under the microscope, the polished surfaces nearly always show the structures described above. The comparatively late appear-

ance of galena should not influence one to classify it as a supergene mineral. Thus, Lindgren¹ states that well-defined zones of supergene lead sulphide have never been observed. Attention has been called, however, to the formation of galena in well-defined crystals up to $\frac{1}{2}$ inch in size, on iron spikes in old mine workings.² While this would suggest the possibility of its deposition by superegene solutions, it should be remembered that, lacking other evidences, the striking and unusual occurrence should not be taken as criteria in the natural deposition of ores. Irving and Bancroft,³ on the other hand, state positively that a portion of the galena at Lake City, Colorado, is connected with oxidation processes.

Even before the microscopic study of polished surfaces of ores, it was appreciated that galena unaccompanied by definite silver minerals was notably lean in silver. Thus, in the silver deposits of Bingham, Utah, Boutwell⁴ found those ores to assay highest in silver which contained the largest amount of some silver mineral—in this case, tetrahedrite. The pure galena samples were the leanest of all. In the silver deposits near Lake City, Colorado, Irving and Bancroft⁵ report that “little of the argentiferous galena is rich in silver in any of these districts unless accompanied by tetrahedrite or some rich secondary mineral.” In this case, surfaces were roughly polished, and, when found to be homogeneous, the assay values did not exceed 10 to 15 ounces of silver per ton. Some years ago, the writer examined a large number of polished surfaces of galena from different sources, for the purpose of determining the limit of solubility (or isomorphism) of silver sulphide or other silver minerals in natural galena. The procedure consisted in examining the surface with high magnification and counting the spots, removing a small amount of the specific area thus studied, and determining the silver. It was found that all areas of galena containing more than 0.10 per cent silver showed an appreciable number of spots of either argentite or tetrahedrite, frequently both. When the

¹ LINDGREN, “Mineral Deposits,” p. 876, 1919.

² WHEELER, “Rapid Formation of Lead Ore,” *Am. Inst. Mining Eng.*, Vol. LXIII, p. 311, 1920.

³ IRVING and BANCROFT, “Geology and Ore Deposits near Lake City, Colo.,” *U. S. Geol. Sur., Bull.* 478, p. 97, 1911.

⁴ BOUTWELL, “Economic Geology of the Bingham Mining District,” *U. S. Geol. Sur. Prof. Paper*, 38, p. 113, 1905.

⁵ IRVING and BANCROFT, *op. cit.*

spots were very numerous, but still very small, the silver content might reach 0.39 per cent silver. Only when numerous and of considerable size was the percentage raised to 0.50 per cent silver. In this investigation, the spots were frequently so small that many of them could not be identified, and it seems quite probable that some of them do not contain silver. In Fig. 5 is illustrated an etched surface of galena from Rimini, Montana, in which spots of four distinct minerals could be recognized.

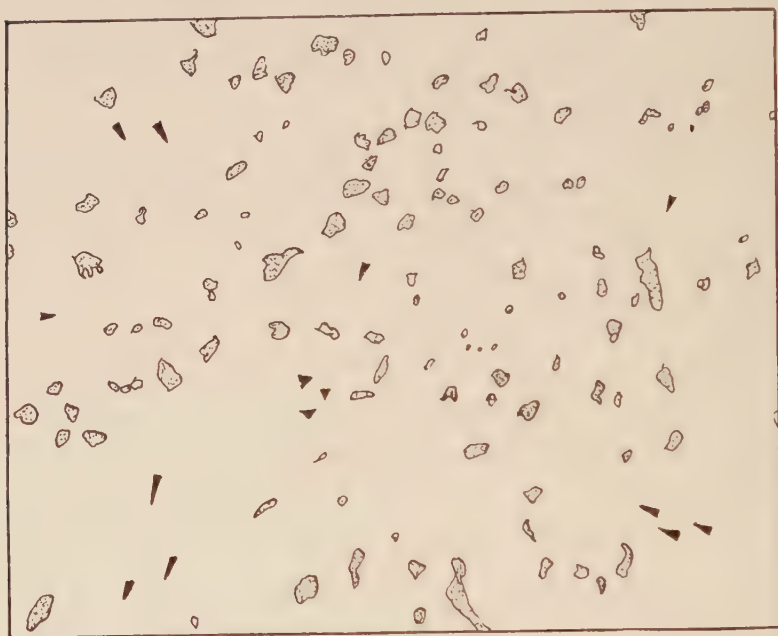


FIG. 5.—Galena (white) showing spots of various silver minerals (dotted). Rimini, Montana. Galena does not hold in solid solution or homogeneous mixture large quantities of argentite or other silver minerals. Consequently, if appreciably argentiferous, it reveals that fact microscopically by the presence of numerous spots often of several different silver minerals. $\times 268$.

One mineral harder than galena was identified as tetrahedrite. The other three were all softer; one was identified as proustite by its bluish tint in reflected light, the third was thought to be argentite, while the fourth could not be determined. It was probably some sulphosalt of silver or lead. Thus, it seems to be demonstrated that galena under natural conditions cannot hold large quantities of silver sulphide or other silver minerals in the state of solid solution or isomorphous mixtures. If silver is

present in any considerable quantities (above 0.10 per cent), the fact is revealed by the microscope. This is quite different from the condition of silver in tetrahedrite, where it is undoubtedly an isomorphous mixture. As to the origin of these spots, there still remains considerable uncertainty. The extremely small ones do not appear like later additions and are, therefore thought to be segregations of impurities which were originally still more disseminated in the galena. Some of the spots are residual grains of tetrahedrite left over after replacement by galena has occurred.



FIG. 6.—Pyrrargyrite following cleavage cracks in galena (white). Sandon British Columbia. Undoubtedly an enrichment or later addition. A few spots of silver minerals also appear. These may have a different origin from the veinlets and may represent an unmixing phenomenon. $\times 343$.

Occasionally, the inclusions of rich silver minerals appear definitely as later additions. Then they take on more definite shapes, rods and even small veinlets being abundant. A case of such undoubted enrichment is shown in Fig. 6, where pyrrargyrite is seen following cleavage cracks in galena. Although this represents conclusive evidence of later addition of the later rich silver mineral, there are no data available which might assist us in deciding whether the enrichment is hypogene or supergene.

These occurrences do not differ essentially from the veinlets of the same minerals found in arsenopyrite, sphalerite, and tetrahedrite. Unless there is some evidence of oxidation processes, as shown by the presence of definitely established supergene minerals or unless there is satisfactory field evidence, we cannot be sure of the supergene character of these enrichments.

The experiments mentioned above confirm the laboratory results of Nisson and Hoyt¹ on dry melts of mixtures of lead and silver sulphides. They found that lead sulphide when fused was capable of adsorbing or holding in solid solution on cooling, less than 0.20 per cent silver sulphide. An excess above that always separated out as definite grains of argentite similar to the natural occurrences described above. Of course, these two cases are not exactly parallel, unless we except the theory held by some that such ore bodies have been formed by the injection of melted material. We can only say that for the two cases the final equilibrium results seem to be about the same.

REPLACEMENT PROCESSES IN THE ASSOCIATED COPPER SULPHIDES

Chalcopyrite.—Perhaps the most characteristic place of chalcopyrite in the silver-lead ores is just after tetrahedrite and before galena. Galena often contains residual grains of chalcopyrite showing good replacement borders with respect to the later lead mineral. Chalcopyrite is often definitely later than tetrahedrite, appearing in the form of stringers and wandering veinlets which do not tend to enlarge into great masses. Some of these may be simply filling of fractures. These occurrences, being earlier than galena, which is firmly believed to be hypogene, definitely place this generation of chalcopyrite as also hypogene. A later generation of chalcopyrite is also observed mainly in the form of thin veinlets following cleavage directions in galena. The borders are very smooth and straight, and little or no replacement seems to have taken place. They are probably merely crack fillings and may represent simply a local resolution of the earlier chalcopyrite. Here, again, it does not seem to be necessarily connected with the alteration products

¹ NISSON and HOYT, "Silver in Argentiferous Ores," *Econ. Geol.*, Vol. X, p. 172, 1915.

of galena, such as cerussite and anglesite and may, therefore, still be hypogene.

From the standpoint of silver deposits, we might summarize the occurrence of associated chalcopyrite somewhat as follows:

1. Blebs in pyrite, sometimes very rare and inconspicuous. This is the earliest appearance of copper in the vein as a recognizable mineral, before copper enrichment has taken place.

2. As dots, sometimes of extremely small size, and small laths in sphalerite. This is thought by many investigators to be an unmixing or segregation from a solid solution.

3. As a generation earlier than the argentiferous galena.

4. As a generation later than galena. Much of this is undoubtedly supergene.

5. Replacing the later silver minerals, as argentite, polybasite, etc. Here it occurs as minute wandering veinlets probably of little paragenetic importance.

6. As darts in bornite following crystallographic directions. This, also, is held by many to represent an unmixing phenomenon.

In case copper is somewhat abundant in the silver vein, chalcopyrite may, in addition to the minor characteristics mentioned above, occur replacing pyrite and further altering to bornite and chalcocite, thus giving rise to the well-known series in copper enrichment.

Bornite.—This is not so common an associate of the silver minerals as chalcopyrite and becomes interesting only in deposits similar to the Silver King Mine in Arizona, where the copper minerals are especially persistent. In this mine, as mentioned previously, all of the processes of copper enrichment, probably mainly hypogene, are observed parallel with a progressive enrichment of the silver minerals. In this procedure, stromeyerite sometimes makes its appearance in the place of chalcocite and shows similar replacement effects with respect to bornite. In Fig. 7, illustrating a polished specimen from the Silver King Mine, Arizona, is seen a sort of graphic intergrowth of bornite and stromeyerite. The structure is believed to be due to replacement, as there seem to be connecting veinlets and the borders sometimes show characteristic replacement structures. In the same specimen, stromeyerite is found to be replacing tetrahedrite in a most intricate network of veinlets (Fig. 9).

Bornite from the Cobalt district, Ontario, has been replaced by native silver, as shown in Fig. 8. This occurrence, which

was published as a photomicrograph in 1917,¹ was associated with large areas of native silver together with traces of oxidation products of copper and was, therefore, thought to be supergene. Schneiderderhöhn,² on the other hand has interpreted this photomicrograph as another case of unmixing or *emulsion*.



FIG. 7.—Stromeyerite probably replacing bornite in a design somewhat resembling the so-called graphic structures. Silver King, Arizona. Stromeyerite, dotted. Bornite, white. Quartz, lined. Holes, black. Note connecting-veinlets between many of the stromeyerite areas, as well as the borders around quartz grains. These features strongly suggest replacement. $\times 81$.

Chalcocite.—This mineral when found associated with the rich silver ores may show the same replacement phenomena as in the typical copper deposits. It is seen replacing the older sulphides of copper and iron as pyrite, bornite, and chalcopyrite. It does not seem to replace the rich silver minerals but, so far as they are concerned, seems to be associated most frequently

¹ GUILD, "A Microscopic Study of the Silver Ores and Their Associated Minerals," *Econ. Geol.*, Vol. XII, p. 297, 1917.

² SCHNEIDERHÖHN, "Entmischungerscheinungen innerhalb von Erzmischkristallen und ihre Bedeutung für Lagerstättenkunde und Aufbereitung," *Metall. u. Erz*, Vol. XIX, p. 526, 1922.

with stromeyerite and native silver. It is, therefore, found in irregular patches with bornite and showing contacts without definite relations; as the frequently described intergrowths with bornite; and as veinlets extending in all directions in bornite and chalcopyrite. The last-mentioned occurrence is frequently associated with quartz occupying the center of the chalcocite veinlet. This quartz is sometimes stained with



FIG. 8.—Native silver (dotted) replacing bornite. Cobalt, Ontario. Structures like this are held by some as always representing an unmixing of solid solutions. This is believed, however, to show a real case of enrichment as larger masses of silver in the same material appear as veinlets and other characteristic replacement structures. $\times 506$.

malachite and bordered by leafy replacements of covellite. Such features are thought to be definite evidence of supergene deposition. These characteristics of copper deposition are mentioned because they may all be observed in the very same specimen in which appear an accompanying enrichment of silver. They may, therefore, serve to throw light upon the less-known processes of silver deposition. In some cases, the two lines of enrichment interpenetrate, as when bornite, for example, is replaced by either chalcocite or the silver-copper mineral stromeyerite.

PARAGENESIS OF THE TYPICAL SILVER-ORE MINERALS

Tetrahedrite.—This mineral when argentiferous (freibergite), as mentioned above, is not thought to be an enrichment product of leaner tetrahedrite or other silver minerals. Rather it is to be considered as one of the earliest starting points to be detected by the microscope in the later complex enrichment processes. It is, thus, seen to break down and give rise to areas or zones of enrichment products. These may appear as crystallizations of

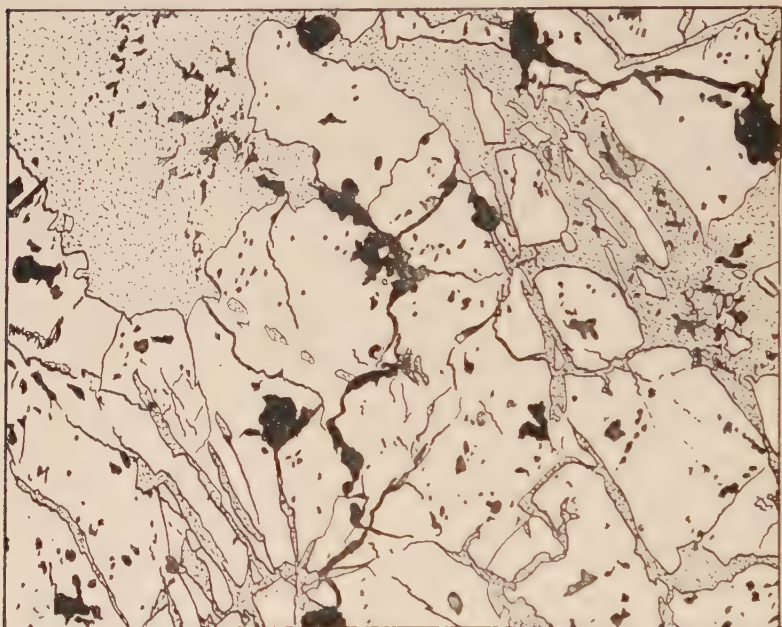


FIG. 9.—Stromeyerite (dotted) replacing tetrahedrite in a complex network of veinlets. Silver King, Arizona. The tetrahedrite itself contains considerable silver yet it is invisible as it occurs as an isomorphous mixture. The presence of the stromeyerite certainly represents a later silver enrichment of the earlier ore mineral. The silver may be derived, therefore, either from lean tetrahedrite or from other and perhaps still leaner silver bearing ores. $\times 76$.

new minerals, as proustite, pyrargyrite, stromeyerite, etc., or as spots, veinlets, and cavity fillings in the original tetrahedrite to be seen only by means of the microscope. In the last-mentioned case, if the original tetrahedrite contains but a small amount of silver, the *enrichment* may be considerable. In Fig. 9, traced from a photograph of a polished specimen from the Silver King Mine, Arizona, may be seen tetrahedrite crossed

by a fine network of stromeyerite veinlets. There seems to be no valid reason for not assuming that other areas of pure stromeyerite in the same specimen, or, in fact, in the same deposit but unassociated with tetrahedrite, have the same origin, *viz.*, the replacement of tetrahedrite. Tetrahedrite with veinlets of proustite and pyrargyrite has also been frequently observed. As all of the constituents for the formation of the ruby silvers, as



FIG. 10.—The later silver minerals, proustite and pyrargyrite, filling drusy cavities in quartz. Tonopah, Nevada. Pyrargyrite, dotted. Proustite, white. Quartz, broken lines. Pyrargyrite is deposited first around euhedral quartz crystals, the center of the cavity being later occupied by proustite. The contact between the two ruby silvers has always been found sharp. $\times 75$.

well as stromeyerite, are found in tetrahedrite, they all may be formed rather directly from the breakdown of the earlier mineral. Chemical reactions may easily be devised showing how this might take place.

The Ruby Silvers.—The microscope does not show these two minerals, pyrargyrite and proustite, to be isomorphous, as might be expected. Whenever associated with each other, they show sharp boundaries, and the gradual passing of one into

the other which would indicate isomorphism has not yet been observed under the microscope. Sometimes they are found in rather definite sequence, as shown in Fig. 10, taken from a specimen from Tonopah, Nevada, where cavities have been filled by these two minerals, probably by supergene solutions. Proustite has been deposited first around the borders of drusy cavities, the center being later occupied by pyrargyrite. On the other hand, perhaps the more frequent occurrence is that of a most intricate intermingling of the two components. Whether these were homogeneous at the time of deposition and, thus, represent a case of unmixing cannot be definitely stated. No particular pattern has been observed, as is usually true in such cases. Microscopic investigation thus confirms the crystallographic and chemical studies of Miers,¹ who also concludes that these two minerals form distinct species and are not perfectly isomorphous.

The majority of the early descriptions seem to place these minerals as supergene. Thus, Ransome² held that many of the rich silver minerals, especially proustite, are probably as characteristic of downward enrichment as chalcocite. Bastin and Laney³ regarded pyrargyrite as both hypogene and supergene at Tonopah, Nevada, corresponding to their two types of the mineral. The hypogene variety was found in veinlets as replacements in brecciated quartz and sericitized wall rock. In Chañarcillo, Chile, according to Whitehead:⁴

. . . the availability of the ore shoots to mining has been due to replacement of the predominant primary sulphides, pearcite, proustite, and pyrargyrite, by argentite, dyscrasite, and native silver. This enrichment was apparently brought about by supergene processes.

The microscope certainly shows the ruby silvers crossing in fine veinlets, all of the earlier ore minerals beginning with arsenopyrite and ending, perhaps, with galena. How many of these occurrences represent hypogene deposition constitutes one of the

¹ MIERS, "Contribution to the Study of Pyrargyrite and Proustite," *Mineralog. Mag.* 8, p. 57.

² RANSOME, "Criteria of Downward Sulphide Enrichment," *Econ. Geol.*, Vol. V, p. 211, 1910.

³ BASTIN and LANEY, "The Genesis of the Ores at Tonopah, Nev.," *U. S. Geol. Sur. Prof. Paper*, 104, 1918.

⁴ WHITEHEAD, "The Veins of Chañarcillo, Chile," *Econ. Geol.*, Vol. XIV, p. 1, 1919.

difficult questions of silver-ore genesis. There may be, however, a too-great tendency to interpret such structures as mentioned above, *viz.*, the crossing of the early minerals by the later, as due to downward enrichment.

The occurrence of ruby silvers as spots and veinlets in galena has already been described (Fig. 5). In Fig. 11 is seen a beautiful intergrowth between proustite and galena, the whole being a remnant in a pyrargyrite area. This was observed in a

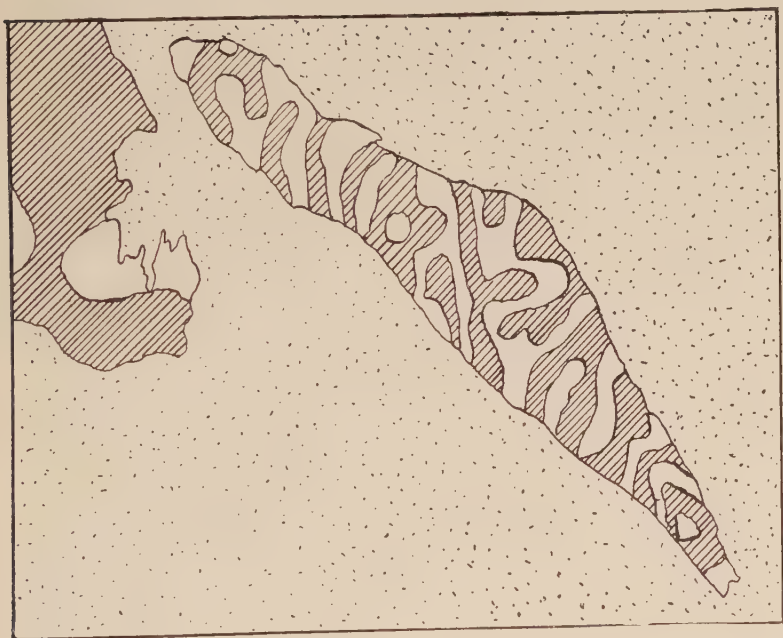


FIG. 11.—A galena-proustite intergrowth appearing as a small residual grain in pyrargyrite. Schemnitz, Hungary. Galena, white. Proustite, lined. Pyrargyrite, dotted. $\times 1,174$.

specimen from Schemnitz, Hungary. The common appearance of the ruby silvers as breakdown products of tetrahedrite has already been mentioned. They they appear as spots and wandering veinlets in tetrahedrite as well as in the associated minerals.

Argentite.—From the numerous descriptions of the occurrence of this mineral, it would seem that it may be either hypogene or supergene. Thus, great masses were found in the upper zones of the Comstock Lode. Such bonanzas usually occur directly

under the oxidized zone, and the evidence seemed to be conclusive that they had been deposited by supergene solutions. Yet in the Comstock Lode, argentite has been identified at a depth of 3,000 feet below the surface.¹ Recently, Bastin² has restudied these ores, employing the reflecting microscope, his work including material to 2,900 feet in depth. As a result, he has come to the conclusion that "including the bulk of the bonanza ores of the lode the silver is essentially all in primary minerals." Above 500 feet, descending solutions of surface origin have produced important enrichment, although, in this zone, some of the silver is also in primary minerals. In the Tintic mining district, according to Lindgren and Loughlin,³ argentite is not a rare mineral but cannot easily be identified without the microscope, as it occurs in minute grains in the galena. In this form, it is thought to be primary. But when found associated with gold and cerargyrite, it is held to be undoubtedly supergene. At Tonopah, Nevada, also, some occurrences are held to be primary while others are thought to be secondary. Many other examples might be given showing abundant evidence to support the view that argentite may sometimes be hypogene and at others, supergene.

In the microscopic study of argentite ores, we are disappointed not to find more characteristic structures that might shed light upon the subject of its paragenesis. It has rarely been seen definitely replacing the other sulphides or, in fact, any of the associated minerals. An exception to this rule was observed in a specimen from Cobalt, Ontario, where argentite was found apparently replacing smaltite in a system of complex veinlets (Fig. 12). Even here, as the smaltite shows euhedral surfaces against the argentite, doubt has been cast upon the usually accepted sequence.

Argentite, on the other hand, yields easily to attacking solutions, probably mainly supergene, and breaks down readily into native silver. Almost every specimen studied showed this tendency to a greater or lesser degree. One specimen from Butte,

¹ EMMONS, "The Enrichment of Ore Deposits," *U. S. Geol. Sur. Bull.* 625, p. 274, 1917.

² BASTIN, "Bonanza Ores of the Comstock Lode, Virginia City, Nev.," *U. S. Geol. Sur. Bull.* 735, p. 41, 1922.

³ LINDGREN and LOUGHLIN, "Geology and Ore Deposits of Tintic Mining District," *U. S. Geol. Sur., Prof. Paper* 107, 1919.

Montana, showed thousands of minute spots of silver of such extremely small dimensions as to be seen only under very high magnification. Other specimens showed delicate, wandering veinlets.

Stromeyerite.—In the silver ores thus far investigated, stromeyerite seems to present two modes of occurrence: (1) as a replacement or enrichment product of tetrahedrite. This is shown in Fig. 9, from the Silver King Mine, near Superior,



FIG 12.—Veinlet of argentite (dotted) in Smaltite (white). Cobalt, Ontario.
×64.

Arizona, where it appears as a complex system of veinlets crossing tetrahedrite. In the same specimen, it appears as narrow borders lining gangue minerals embedded in tetrahedrite. (2) As a replacement product of bornite, where it shows the same characteristics as chalcocite in similar conditions. Thus, it is found as thin borders and veinlets, as areas containing ragged residual grains of bornite, and as patches mingled with bornite and showing indefinite relations. It has also been observed occasionally in very small particles of ordinary copper ores which were not considered particularly argentiferous.

Stromeyerite is nearly always mixed with an excess of the chalcocite molecule, which does not seem to form solid solutions with the stromeyerite molecule, at least at ordinary temperatures. This causes the surface to lack smoothness and uniformity of color. Stromeyerite in contact with chalcocite appears slightly softer, especially if polished for great relief, and shows a pale lavender tint. While this mixture seems to be very irregular at times, there seems to be some tendency for it to take on definite patterns characteristic of graphic intergrowths or unmixing effects among the alloys. This is shown in Fig. A, Plate I, a photomicrograph of a specimen from the Silver King Mine, Arizona. At first, the cause of this complicated structure was not understood. Finally, however, material was found in which a complete gradation between smooth stromeyerite and chalcocite could be observed. Between the two was a small area showing the structure as here illustrated. A photomicrograph, together with a more complete description may be examined in an earlier contribution.¹ The etch patterns of the chalcocite area here seem to indicate the low-temperature form, in which case, the deposition would be supergene. This particular photomicrograph would also seem to show that the stromeyerite was an enrichment product of the chalcocite. Although, in this work, KCN was used as an etching reagent to bring out the structure, it can easily be seen without and may even be photographed provided the specimen is polished for great relief and the proper ray filter employed. This is illustrated in Fig. B, Plate I, where, it might be mentioned in passing, several other interesting paragenetic features may be observed. This specimen shows the following replacement processes, all but the first mentioned appearing on the reproduction: pyrite, chalcopyrite, bornite, stromeyerite, native silver.

When associated with tetrahedrite, the simplest explanation of the origin of stromeyerite seems to be that already suggested, *viz.*, a breakdown and enrichment of the tetrahedrite molecule. This does not necessarily require addition of new material. When derived from bornite, the natural explanation seems to be that we have a replacement process where both copper and silver solutions are concerned. That the copper molecule should be more or less in excess is to be expected. It may even be

¹GUILD, "A Microscopic Study of the Silver Ores and Their Associated Minerals," *Econ. Geol.*, Vol. XII, 1917.



FIG. A.—Stromeyerite and chalcocite intergrowth. Silver King, Arizona. Etched with KCN. Dark is chalcocite. $\times 98$.

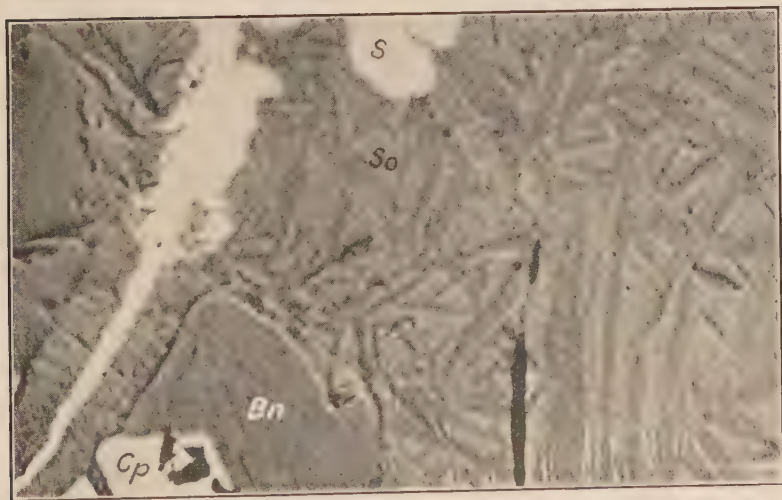


FIG. B.—Stromeyerite (So), bornite (Bn), chalcopyrite (Cp) and native silver (S). Silver King, Arizona. This shows both copper and silver "enrichment" in the same section. $\times 223$.

true that some of the silver is added later (to chalcocite), as might be assumed from the gradational effects described above. In either case, stromeyerite seems to play about the same role as chalcocite in the enrichment of copper ores. Several specimens of stromeyerite have been examined, one from Tasmania, one from Tombstone, Arizona, and others from various other localities in Arizona, in which the surfaces are smooth and develop no complicated structure on etching.

It seems to be definitely proved, then, that stromeyerite is not an isomorphous mixture of copper and silver sulphides but a definite double salt, $\text{Cu}_2\text{S}.\text{Ag}_2\text{S}$. Excess of either the silver or the copper molecule apparently cannot occur without destroying its homogeneity. No fading-off effects have ever been observed between areas of different composition, as might be expected in case of isomorphism or limited solubility. Intergrowths between stromeyerite and galena, galena and chalcocite, and stromeyerite and argentite, almost identical with that illustrated in Fig. 11 between galena and proustite, have often been observed in silver ores. These are believed to represent unmixing phenomena. The two constituents were first deposited as homogeneous or submicroscopic mixtures with later segregations into the complicated structures represented.

Stephanite.—This sulphantimonite is of less importance than the silver minerals thus far studied. It is frequently found in company with the ruby silvers, which it resembles in composition. Thus, it has been described from Freiberg, Germany, as occurring with kernels of pyrargyrite.¹ It seems to show a strong tendency to replace gangue material, as shown by Fenner's (see p. 204) description of an interesting occurrence of this mineral in which the constituents of a rhyolitic rock have been replaced. In one specimen described, chalcopyrite replaced the groundmass, while the stephanite appeared later replacing feldspar phenocrysts. In Fig. 2, already described, stephanite is found replacing the constituents of a brecciated gangue consisting mainly of quartz and calcite.

Polybasite. While this mineral is probably of more importance than stephanite, it is sufficiently rare to make difficult any investigation of its paragenetic features. An occurrence which is, perhaps, rather typical is shown in Fig. 13, from a specimen from Guanacevi, Mexico. This shows a veinlet of

¹ HINTZE, "Handbuch der Mineralogie," Vol. I, p. 1155.

galena with patches of polybasite appearing here and there. Occasionally, there are structures which appear to make it later and replacing galena. It is described by Bastin¹ as a secondary mineral replacing galena. In the Little Belt Mountains, Montana, it has been described as "an alteration product of galena,



FIG. 13.—A veinlet of galena (white) and polybasite (dotted in sphalerite (also white). Guanacevi, Mexico. This shows an enrichment of the early non-argentiferous sulphides by later silver replacements. The sphalerite shows the characteristic spots of chalcopyrite believed by many to represent unmixing of solid solutions. $\times 64$.

and to be mixed with and to grade into pyrargyrite, which in some cases is its undoubted alteration product,"² In specimens from the Seven-thirty Mine, near Georgetown, Colorado, tetrahedrite was found as residual grains surrounded by polybasite in which were found numerous wavy streaks of proustite. These are good illustrations of how this mineral occurs, associated, as it usually is with other sulphantimonites or sul-

¹ BASTIN, "Metasomatism in Downward Sulphide Enrichment," *Econ. Geol.*, Vol. VIII, p. 51, 1913.

² WEED and PIRSSON, "Geology of the Little Belt Mountains, Mont.," Twentieth An. Rept. *U. S. Geol. Sur.*, Part 3, p. 411, 1899.

pharsenites of similar composition. A striking occurrence of polybasite yielding many millions of dollars was found in the Milly Gibson Mine, Aspen, Colorado. According to Lindgren,¹ this certainly suggests enrichment by descending waters; but Spurr holds its origin to be primary.² At Neihart, Montana, polybasite seems to be partly hypogene and the ultimate source of the later silver minerals in the enrichment zones.³ According to Bastin,⁴ the sulphosalts of silver, as pearceite, proustite, etc., are characteristic hypogene minerals in the silver deposits of the San Juan Mountains, Colorado. The microscopic structure seems to suggest deposition contemporaneous with the early sulphides. These same minerals are thought to be supergene in certain places of the same region. According to Burton,⁵ the polybasite at the Premier Mine, British Columbia, is partly hypogene and partly supergene. The hypogene type is confined to rounded blebs in galena and masses intergrown with pyrrhotite filling vugs in quartz or replacing calcite or some of the earlier vug-filling sulphides. The supergene variety is found almost solely replacing tetrahedrite, which occurs in veinlets crossing the older sulphides within 650 feet of the surface.

Native Silver.—When occurring in or near the oxidized zone, there seems to be no doubt that this mineral has been formed by downward enrichment processes. The microscope, furthermore, shows it to be later than the early sulphides and, in fact, usually later than the latest sulphides and sulphosalts found in the vein. It is, however, thought to be primary in the zeolitic copper ores of Lake Superior, and there are many cases on record where it is found at great depths. In the Aspen district of Colorado it is found crossing barite at considerable depth, while at Creede Colorado,⁶ it occurs to a depth of 1,100 feet. These deep occurrences suggest to some the possibility of its occasional hypogene origin. Depth alone should not be taken as a criterion of hypo-

¹ LINDGREN, "Mineral Deposits," p. 612, 1919.

² SPURR, "Ore Deposition at Aspen," *Econ. Geol.*, Vol. IV, p. 301, 1909.

³ HURST, "Supergene Processes at Neihart, Mont.," *Econ. Geol.*, Vol. XVII, p. 382, 1922.

⁴ BASTIN, "Silver Enrichment in the San Juan Mountains, Colo.," *U. S. Geol. Sur. Bull.* 735, p. 65, 1922.

⁵ BURTON, "Ore Deposition at Premier Mine, B. C.," *Econ. Geol.*, Vol. XXI, p. 586, 1926.

⁶ EMMONS and LARSEN, "Geology and Ore Deposits of the Creede District, Colo.," *U. S. Geol. Sur. Bull.* 718, p. 104, 1923.

gene deposition, as it is well known that oxidation takes place in some deposits many hundreds of feet below the surface. Thus, Bastin and Laney¹ found silver 1,400 feet below the surface in the Belmont vein associated with blue-green copper salts. This, of course, shows that oxidizing influences have reached to this depth, and the silver may or may not have been connected with them.

Silver compounds are easily broken down to the metal, and there seems to be no logical reason why native silver should not form remote from surface conditions. As early as 1843, Bischof² found that superheated steam was capable of reducing argentite to metallic silver which appeared as arborescent shapes very much as in nature. Other silver minerals treated in the same way yielded similar results. These experiments have been repeated from time to time with modifications, some even finding that the metal could be formed at 100°. It has frequently been shown in the laboratory that many sulphides and arsenides precipitate silver from silver-sulphate solutions. Chalcocite seems to be one of the best precipitants, and the writer has samples in sealed tubes where crystals of silver have been growing for about 9 years. The crystals are flat tabular but show most brilliant surfaces, and some have reached a length of 7 or 8 millimeters. Crystals formed on galena during the same length of time were equidimensional, showed sharp crystal faces, but reached a diameter of only about $1\frac{1}{2}$ millimeters. Therefore, if hypogene solutions of silver come in contact with such sulphides in nature, there seems to be no reason why native silver should not form. From such considerations as these, Katō³ believes that native silver in certain ore deposits of Japan was deposited by hypogene solutions. More recently, other authors have emphasized the probability of silver deposits being hypogene, as, for example, those near Wickenburg, Arizona.⁴ The evidence is based upon microscopic investigation and rests upon the fact that native silver, as well as proustite and pearceite, has crystallized contemporaneously with several of the commoner and unquestionably

¹ BASTIN and LANEY, "The Genesis of Ores at Tonopah, Nev.," *U. S. Geol. Sur., Prof. Paper* 104, p. 34, 1918.

² BISCHOF, "Einige Bemerkungen über die Bildung der Gangmassen," *Pog. Ann.* 60, p. 285, 1843.

³ KATŌ, "The Ore Deposits in the Environs of Hanano-Yama," *Meiji College of Tech., Jour.*, Vol. I, p. 32, 1916.

⁴ BASTIN, "Primary Native Silver Ores near Wickenburg, Arizona," *U. S. Geol. Sur. Bull.* 735, p. 131, 1922.

primary ore minerals. Bastin has also worked in the laboratory with silver bicarbonate solutions and found them to precipitate silver easily in the presence of nickel and cobalt arsenide. These solutions are evidently considered as more analogous to hypogene solutions than the sulphate of silver more often employed. A still more recent paper¹ by the same author emphasizes further the probable primary nature of silver in the Cobalt district.

In the microscopic investigation of the silver ores, many interesting cases have been observed where silver minerals

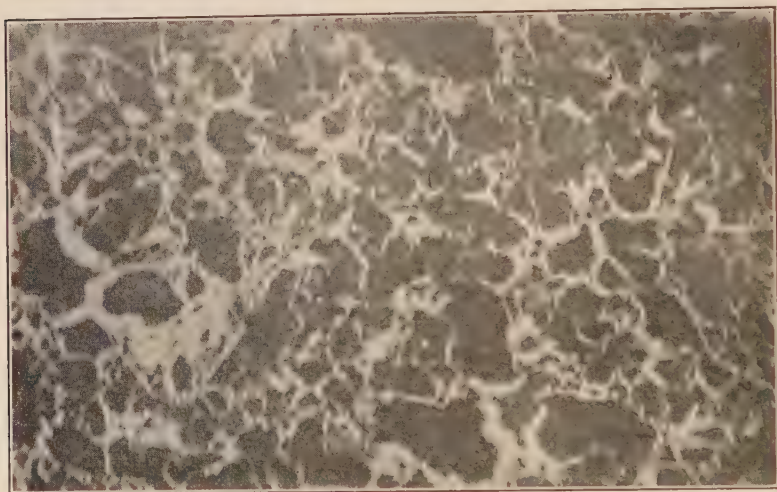


FIG. C.—Chalcocite (dark) and native silver. Silver King, Arizona. This may be a breakdown of stromeyerite or the precipitation of silver by chalcocite. $\times 150$.

have broken down to native silver. The frequent occurrence of spots of silver of extremely small size has already been mentioned. This is the first step, perhaps, in the breakdown of a silver mineral, solution, transportation, and recrystallization being necessary for the production of arborescent forms so often observed. Delicate veinlets of silver are often seen in argentite and, in fact, in almost any silver mineral. Such a veinlet is shown in Fig. B, Plate I, where it appears in stromeyerite associated with copper minerals. Silver associated with chalcocite in the form of beautiful filliform shapes is illustrated in Fig. C, Plate II. This is also from the Silver King Mine in Arizona,

¹ BASTIN, "Primary Native Silver Ores of S. Lorraine and Cobalt, Ont.," *Econ. Geol.*, Vol. XX, p. 1, 1925.

and the chalcocite areas are so intimately associated with stromeyerite that they are thought to be the result of a breakdown of the stromeyerite molecule. It must not be forgotten, however, that chalcocite is a good precipitant of silver and that this structure might also result from silver solutions being brought in contact with the copper sulphide. On etching surfaces similar to that just described, the individual grains of chalcocite are brought out, and the tendency for the films of

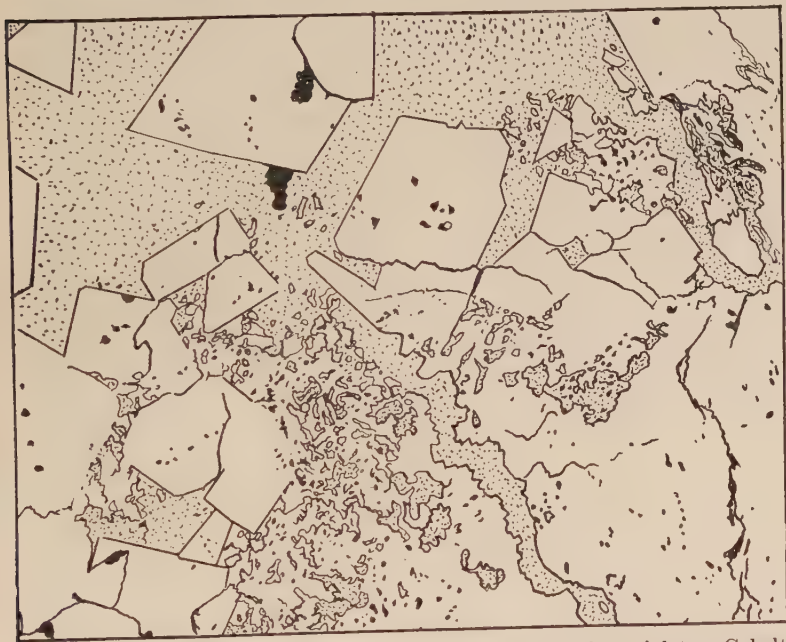


FIG. 14.—Silver (dotted) crossing smaltite (white) in veinlets. Cobalt, Ontario. The tendency of smaltite to show euhedral crystals with reference to silver is illustrated by the sharp isolated crystals as well as the jagged outline of surfaces even those lining the veinlets. $\times 64$.

silver to surround grains and to follow cleavage in the grains of chalcocite becomes more striking. The areas with the filliform structure are sometimes found to grade into stromeyerite, when the native silver is apt to disappear altogether or be confined to borders or a few isolated veinlets. Silver is, also, frequently found as spots and veinlets in tetrahedrite, the ruby silvers, and polybasite. Native silver replacing bornite has already been described and is shown in Fig. 8. Further on, its relation to the arsenides will be briefly discussed. Thus, it

would seem that native silver may replace many of the earlier minerals as well as the later and, in some cases, already enriched products. Many of the associations and replacements are such as strongly to suggest hypogene origin.

THE NICKEL-COBALT-SILVER ORES

Although this type of silver deposit has been the subject of numerous papers since the introduction of the reflecting microscope, it is still as much of an enigma as ever. In the study of some of these deposits, the investigator has been impressed with the intimate intergrowth of smaltite, niccolite, and native silver and has argued in favor of simultaneous deposition. The work of Bastin (see p. 232) along this line has already been mentioned. Even veinlets of silver in smaltite are not thought to be replacements here, since the smaltite walls show their own crystallographic boundaries with reference to the metal (Fig. 14). Others,¹ while holding firmly to the idea of the hypogene nature of the silver, consider it to belong to the last stages of primary mineralization.

Some of the characteristic structures of this type of ores may be outlined briefly as follows:

1. Euhedral crystals of smaltite-cloanthite embedded in native silver (Fig. 14).
2. Concentric arrangement of smaltite and niccolite, with sometimes silver or bismuth or both in the center.
3. Dendritic growths of smaltite in chalcite, the dendrites sometimes consisting of hollow shells arranged in rows and branching, the center being occupied by native silver.
4. Veinlets of silver in smaltite frequently associated with niccolite (Fig. D, Plate II).

The dendritic structure of these ores has recently been attributed by Van der Veen² to the replacement of calcite along cleavage directions. In the case of perpendicular dendrites, it is thought to be the result of deposition along the intersection of rhombohedral cleavage planes and twinning planes of the negative rhombohedron. That the dendritic structure is due to replacement rather than the filling of cavities seems to be proved on examining the dendrites under polarized light in thin section.

¹ WHITEHEAD, "The Veins of Cobalt, Ont.," *Econ. Geol.*, Vol. XV, p. 103, 1920.

² VEEN, VAN DER, "Mineragraphy and Ore Deposition," The Hague, 1925.

Then it may be seen that calcite within the shell may be crystallographically continuous with the areas outside. This is shown by extinctions as well as the continuance of such features as cleavage and twinning bands.

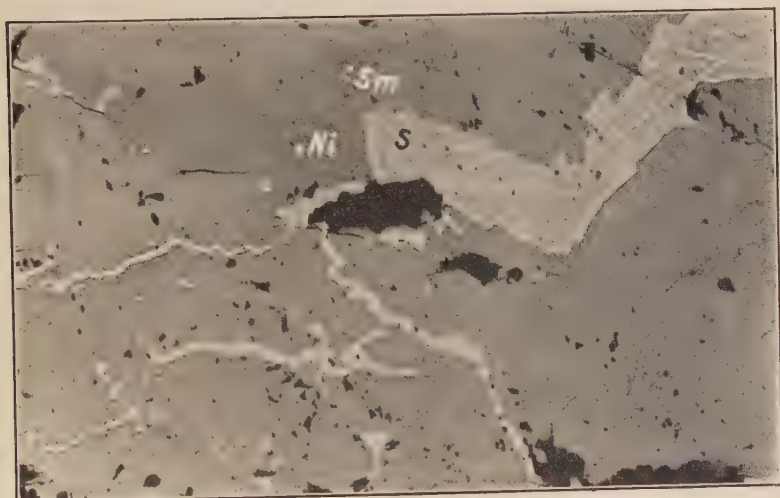


FIG. D.—Silver (S), niccolite (Ni), and smaltite (Sm). Cobalt, Ontario. The silver is probably replacing the niccolite. $\times 102$.

THE HALOGEN-SILVER MINERALS

The *oxidized* minerals of silver are practically limited to the halogen compounds, and they are unquestionably of supergene origin. They result from the action upon the silver minerals of solutions containing the halogens. They are not often found associated with the earlier ore minerals in such a manner as to admit of much microscopic study as to replacement processes or other features. They are found as spots and sheets in oxidized material, usually of very uninviting appearance to the microscopist. As might be expected, cerargyrite, the chloride, is the most common and probably the only one showing any relations to the earlier ore minerals. It has been described as resulting from oxidation processes on argentite, and pseudomorphs after argentite have been mentioned. Without doubt, other early minerals of silver alter in the same manner. When the other halogens are present, we may have some differentiation, the chlorides appearing nearer the surface, just below this in the

chlorobromide zone and, finally, in the iodide zone.¹ Silver chloride is easily reduced, and cases have been described where native silver has resulted in this way. On the other hand, native silver may alter to the chloride. A case of this kind has been observed in specimens from the Stonewall Jackson Mine, Arizona (Fig. 15). That the chloride has been derived from



FIG. 15.—Cerargyrite (dotted) replacing native silver (white) in a gangue consisting mainly of siderite (broken lines). Stonewall Jackson Mine, Arizona. When viewed under lower power these grains are seen to be dendritically arranged. This is taken as evidence of the earlier deposition of the silver. $\times 28$.

the native metal is inferred from the dendritic arrangement of the particles, a feature more characteristic of the metal than cerargyrite. The halogen zone may represent much silver derived from eroded and leached portions of the deposit and may, therefore, be greatly enriched. On the other hand, the

¹ MOESTA, "Ueber das Vorkommen der Chlor-Brom und Jodverbindungen des Silbers in der Natur," Marburg, 1870.

BURGESS, "The Halogen Salts of Silver and Associated Minerals of Tonopah, Nev.," *Econ. Geol.*, Vol. VI, p. 13, 1911. "The Halogen Salts of Silver at Wonder, Nev.," *Econ. Geol.*, Vol. XII, p. 589, 1917.

outstanding feature of the deposit may be a marked barrenness of the outcrop. According to Knopf,¹ this is a characteristic feature of the Divide silver district, Nevada. These phases of the subject, however, are not particularly adapted to microscopic methods.

RESUMÉ

1. The paragenetic features of the silver minerals are largely determined by a study of the associated copper, lead, and zinc minerals. A fairly complete resumé of these has therefore been included in this chapter.

2. Tetrahedrite seems to be the earliest recognizable silver-bearing mineral of the typical silver deposits and, in breaking down, probably becomes the source of many of the later and richer silver minerals, such as pyrargyrite and stromeyerite.

3. Galena probably ranks next as an early silver source, in which case it appears with spots of the silver minerals sometimes of exceedingly small dimensions. When showing no spots, the silver content is not greater than 0.10 per cent silver. This apparently represents the limit of solubility of silver sulphide or other silver minerals in galena under natural conditions.

4. The evidence of some kind of enrichment is present in almost every suite of silver specimens. Notable exceptions are, perhaps, the heavy galena-silver ores, where the silver is confined to microscopic spots and occasional patches of tetrahedrite or argentite.

5. Tetrahedrite shows enrichment processes when replaced by proustite, pyrargyrite, or stromeyerite. Further enrichment may appear when any of these minerals later break down into native silver.

6. Galena, in addition to the microscopic spots of silver minerals mentioned above, may further show enrichment by a later addition of proustite, polybasite, and other minerals with high percentages of silver.

7. Silver solutions coming in contact with chalcocite or other copper mineral may precipitate silver, thus giving rise to considerable enrichment. Under these conditions, stromeyerite may also form, when it plays the same role as chalcocite in copper enrichment.

¹ KNOFF, "The Divide Silver District, Nev.," *U. S. Geol. Sur. Bull.* 715, p. 147, 1921.

8. Perhaps all of the common silver minerals, with the exception of the halides, and even including native silver, may frequently be of hypogene origin. We hold that there is no criterion based on structure alone by which the hypogene or supergene character of the silver may be determined. There seems to be a quite definite sequence of minerals from the earlier sulphides to the later ore minerals, and it is impossible, in many instances, to say where hypogene processes cease and supergene enrichment begins.

9. The greater importance now given to hypogene solutions in the deposition of ore minerals may help to encourage exploitation in primary or hypogene zones which otherwise might be neglected by reason of the lack of downward enrichment processes.

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CHAPTER XII

ZONAL DISTRIBUTION

BY ERNEST E. FAIRBANKS

The zonal theory of ore deposition is a broad generalization based exclusively upon field observations. While the zones consist of different mineral assemblages and, therefore, their interpretation rests primarily upon accurate mineral identification, it is obvious that the commonly found variations in mineral character occurring on a small scale would be confusing if considered in connection with a zonal theory. Nevertheless, the first intimation of a passage from one zone to another may be indicated by a difference in mineral character. For this reason, it is considered advisable to include a brief statement of the zonal theory. A study of the literature on this subject discloses the fact that beyond a somewhat obscure recognition of the existence of mineral zones—analagous to a futurist picture of nature—little is definitely known. We may expect great developments of the zonal theory as research progresses in which physical-chemical methods are combined with petrographic methods by that rare type of geologist who can visualize the problem in all its geological bearings.

The best reconstructed vein system from near batholith roof to surface appears to be that presented by Emmons.¹ This ideal vein system would have a vertical range of several miles, and but few of the indicated zones would ordinarily be encountered. A horizontal zonal arrangement also occurs in which the changes outward from the intrusion are commonly the reverse of those in the vertical succession. Emmons has constructed his succession from batholith roof to surface from a study of the horizontal arrangement. His hypothetical ideal vein system was presented as follows;

¹ EMMONS, W. H., "Primary Downward Changes in Ore Deposits," *Trans. Am. Inst. Mining Met. Eng. Pamphlet* 1319-M, March, 1924.

Surface:	
Barren	1. Barren zone, chalcedony, quartz, barite, fluorite, etc. Some veins carry a little mercury, antimony, or arsenic.
Mercury	2. Quicksilver veins, commonly with chalcedony, marcasite, etc. Barite-fluorite veins.
Antimony	3. Antimony ores—stibnite often passing downward into lead, with antimonates. Many carry gold.
Gold	4. Bonanza ores of precious metals. Argentite, antimony, and arsenic minerals are common.
Silver	Silver minerals, some copper, lead and zinc sulphides, quartz, calcite, rhodochrosite, adularia, alunite, etc.
Barren	5. Most nearly consistent barren zone, represents the bottoms of many tertiary precious-metals veins. Quartz, carbonates, etc., with pyrite and small amounts of other sulphides.
Silver	6. Argentite veins, complex antimony silver sulphides, stibnite, etc. Galena veins with silver. Commonly silver decreases with depth. Quartz gangue, siderite common, often increasing with depth.
Lead	7. Galena veins, commonly with some silver. Sphalerite generally present, increasing in depth. Chalcopyrite common. Gangue is quartz and often carbonates (ferrum, manganese, calcium).
Zinc	8. Sphalerite veins with some lead and chalcopyrite, quartz, gangue.
Copper	9. Tetrahedrite veins, commonly argentiferous, chalcopyrite, present. Some pass downward into chalcopyrite. Enargite veins generally with tetrahedrite and tennantite.
Copper	10. Chalcopyrite veins, generally with pyrite, often with pyrrhotite. The gangue is quartz and in some places carbonates. Some pass downward into pyrite and pyrrhotite with a little chalcopyrite. Generally carry silver or gold.
Gold	11. Gold veins with quartz, pyrite, and, commonly, arsenopyrite and chalcopyrite. At places zones 10 and 11 are reversed.
Bismuth	12. Bismuthinite and native bismuth with quartz, pyrite, etc.
Arsenic	13. Arsenopyrite with chalcopyrite and often tungsten ores.
Tungsten	14. Tungsten veins with quartz, pyrite, chalcopyrite, pyrrhotite, etc. Arsenopyrite is commonly present.
Tin	15. Cassiterite veins with quartz, tourmaline, topaz, etc.
Barren	16. Quartz with small amounts of other minerals.

Several geologists attempting to apply the zonal theory have arrived at the conclusion that one or more of the zones may be lacking in any individual vein. What geologist has not noticed that a certain mineral association at one locality may have a

relatively abundant amount of a rare element present, while, elsewhere, this rare element appears to be missing although the mineral association is essentially the same? This difference has been ascribed to the absence of the particular element in the original magma or submagma.

Lindgren¹ states that

The order of deposition is not simply a function of temperature. The precipitation is a function of temperature, pressure, time, concentration and accompanying components in the system. Therefore any *dictum ex cathedra* regarding the succession in vertical zones will be difficult or even impossible.

The zonal theory is receiving an increasing amount of attention. Laboratory investigations will aid by accurate mineral determinations. Since it has been either very difficult or impossible to identify many of the ore minerals in the past, before the advent of the reflecting microscope, unquestionably many errors of mineral identification exist in the literature. The writer, for example, found benjaminite to be a mixture of aikinite and matildite.² Errors of this kind must be corrected before generalizations based on mineral assemblages can be held valid.

¹ LINDGREN, WALDEMAR, "Magmas, Dikes and Veins," *Trans. Am. Inst. Mining Met. Eng. Pamphlet* 1575-I, June, 1926, p. 17.

² Unpublished paper.

CHAPTER XIII

ORE-DRESSING MICROSCOPY

BY G. M. SCHWARTZ

Introduction.—The application of microscopic study, particularly of polished surfaces of ores, to the study of milling problems has not been so general as might be desired. This has been partly due to the highly specialized nature of the work, to the lack of required equipment, and to a failure to realize the value of such studies. The metallurgists have usually depended upon chemical analyses and assays for a knowledge of the ores, but it is obvious that this gives little information on the mineral composition and none at all on the manner of association. The size of grain and the relation of minerals to each other are the first things to be considered in any concentrating problem.

Some use has long been made of polarizing and binocular microscopes, but the use of the reflecting microscope in ore dressing has naturally followed the development of its use in the study of mineralogical and geological problems of ores. This type of work was introduced in America by Campbell, in 1906.

The first exhaustive study which emphasized the value of mineragraphy from a metallurgical standpoint was by Singewald,¹ who published his results in 1913, and was on the titaniferous iron ores of the United States. Others, especially the members of the staff of the United States Bureau of Mines, and Thomson at Toronto, have since contributed papers; but more data are desirable.

This chapter is, for the most part, limited to the use of reflected light, since a much more exhaustive treatise would be necessary to cover the entire subject of ore-dressing microscopy. The references listed in the footnotes should be carefully studied by anyone attempting practical work of this type.

Equipment.—The equipment necessary for a study of ore-dressing problems is practically the same as that used for

¹ SINGEWALD, "The Titaniferous Iron Ores in the United States," *U. S. Bur. Mines Bull.* 64, 1913.

geological microscopic work. For special types of work, small accessories are often desirable but not essential. A binocular microscope is most useful for examining powders and unmounted grains without polishing. An ocular fitted with a Whipple net ruled micrometer disc is very useful for quantitative work such as the determination of the proportion of various minerals in a crushed ore.¹

A cross-ruled ground glass fitted in the photographic camera may serve the same purpose.² Photographic apparatus and a camera lucida are invaluable in preparing a report but are not necessary if the metallurgist makes his own examinations. For occasional work, it is undoubtedly cheaper and more satisfactory to have the work done by someone of experience and with equipment available.

Preparation of Material and Methods of Study.—In the study of milling problems by use of the reflecting microscope, there are two main methods of preparing the material, depending on whether lump ore or crushed and ground material is to be utilized.

The first method of mounting³ consists of stirring the crushed material in molten sealing wax contained in a pasteboard mold of convenient size. This is simple and, in most cases, gives excellent results. A variation has been used by the author when only a few grains are available. These are spread on a glass plate. A piece of sealing wax of the desired size is heated carefully on one side until quite soft and is then pressed down on the grains and glass. The glass may then be warmed, if necessary, to allow a complete embedding of the grains. A mixture of sealing wax and balsam has been used by others.⁴

¹ HEAD, R. E., "Quantitative Microscopic Determination of Chalcopyrite, Chalcocite, Bornite and Pyrite in a Porphyry Ore," *Repts. of investigations*, U. S. Bur. Mines 2,257, 1921.

FAIRBANKS, E. E., "Microchemical Analysis and Its Application in the Determination of *Low-grade Ores*," *Repts. of investigations*, U. S. Bur. Mines 2,613, June, 1924.

HEAD, R. E., "Ore Dressing Microscopy for Examination of Grain Size in Complex Ore," *Mining Met.*, pp. 17-18, January, 1925.

² FARQUARHARSON, R. W., "Petrology and Its Application in Industry," *Geol. Survey W. Australia*, "The Mining Handbook," pp. 4-5, 1919.

³ HEAD, R. E., *op. cit.*, 1921.

⁴ THOMSON, E., "Mineralography as an Aid to Milling," *Am. Mineralogist*, Vol. VIII, pp. 99-104, 1922.

A new method has recently been described by Head,¹ utilizing redmanol, a powdered resin, which melts at 104°C. A mixture of redmanol and sulphides in the ratio of 3:10 is placed in a mold and subjected to heat and pressure, resulting in a very hard cake which has decided advantages over sealing wax, especially in being unaffected by most reagents.

A very permanent mount has been described by Thomson,² who used sealing wax in brass containers. A small brass ring is used to confine the powder to a small area, and the small ring is subsequently mounted in a brass rectangle of the standard size designed at Harvard and described by Short.³

After mounting, the material is polished in the same manner as masive ore.

Information Obtainable.—Some of the most useful kinds of information obtainable by microscopic studies, and their bearing on problems of ore dressing, are listed in the following outline:

1. Identification of minerals in the ore
 - a. Ore minerals:
 - Flotability
 - Magnetic properties
 - Specific gravity
 - Complex minerals
 - b. Valueless metallic minerals such as pyrite, pyrrhotite, etc.
 - c. Gangue minerals
2. Textural relations
 - a. Size and interrelation of various ore minerals
 - b. Size and relation of valuable to valueless minerals
3. Quantitative data
 - a. Relative amounts of ore and gangue minerals
 - b. Percentage of each ore mineral
 - c. Approximate chemical composition from mineral measurements and average analyses.

Other questions may arise in particular cases, and careful study usually results in information of value. The bearing of the

¹ HEAD, R. E., "A New Method of Preparing Briquetted Mineral Grains for Microscopic Study," *Eng. Mining Jour.-Press*, Vol. CXIX, pp. 889-890, 1925.

² THOMSON, E., "A New Method of Mounting Polished Sections of Mill Products," *Trans. Can. Inst. Mining Met.*, Vol. XXIX, 1926.

³ SHORT, M. N., "The Preparation of Polished Sections of Ores," *Econ. Geol.*, Vol. XXI, pp. 648-664, 1926.

above information on problems of ore dressing may best be shown by a number of specific examples.

APPLICATION OF INFORMATION

1. Identification.—It is obvious that a knowledge of the minerals present in an ore leads to a more intelligent use of metallurgical methods. Since the study of polished surfaces of ores was introduced, it has been found that a megascopic examination gives far from complete knowledge of the mineralogy. Some of the more specific values of an accurate knowledge of the mineralogy are listed in the outline above.

a. Ore Minerals.—Some ores consist mainly of one mineral; in this case, there is not likely to be a metallurgical problem. More commonly, several minerals are present, and the separation is usually difficult in proportion to the number of minerals.

Flotability.—Some ores contain several minerals of the same metal. This is particularly true of copper, and, consequently, problems in flotation arise. In a case described by Head,¹ the copper ore consisted of pyrite, chalcopyrite, chalcocite, and bornite. In crushed material, three groups of mineral particles were found: (1) free grains of each mineral; (2) grains with all three copper sulphides; (3) grains consisting of equal parts of two copper minerals. Regarding this material, Head says:

The grains of free mineral particles were perhaps the most numerous, taking the ore as a whole, but it was noticeable that of the grains of combined or associated sulphides, those grains in which the core is composed of chalcopyrite, with or without bornite, and entirely surrounded by chalcocite were the most numerous in the material up to and including the 100-mesh size. As the ore is crushed finer more of these intimately associated mineral grains are, of course, broken down into individual particles. These occurrences of the copper sulphides should be borne in mind when their relative flotability is considered, since these grains that have a core of chalcopyrite surrounded by chalcocite might logically be expected to behave the same as those composed entirely of chalcocite under like conditions of flotation. Similarly a grain with a core of chalcocite and having a shell of chalcopyrite would probably act in the same manner as a grain composed entirely of chalcopyrite. The possible behavior of grains containing the other mineral associations described, as regards relative flotability, also presents itself for consideration, but will not be discussed here.

¹ HEAD, R. E., *op. cit.*, 1921.

The binocular microscope has also been utilized in a study of flotation problems. In a problem studied in detail,¹ it was found that a given molybdenite ore could be most economically concentrated to a 75 per cent product. Attempts to obtain a higher-grade product would entail too great a loss of value due to the interlocking of grains of molybdenite with quartz, which would not float.

Magnetic Properties.—Magnetic concentration has become increasingly important in recent years, and, thus, added emphasis has been given to minerals other than magnetite which have a greater or lesser degree of magnetism. A case in which a lack of knowledge of the minerals in an ore caused much unnecessary experimentation was the treatment of the contact metamorphic deposits of iron ore at Fierro, New Mexico.² Sulphides in considerable amounts are encountered in the iron ore and cause difficulty in keeping the sulphur content below the allowable maximum. A series of tests of magnetic concentration by which it was hoped to raise the grade of the ore and save the copper were unsuccessful. Microscopic examination of polished specimens showed the presence not only of pyrrhotite but also of chalmersite (cubanite, CuFe_2S_3), a decidedly magnetic copper sulphide (see Fig. 1). This at once eliminated the possibility of magnetic concentration and indicated flotation as the only means of separation, a process not warranted by the price of iron ore. Much experimentation could have been avoided by a preliminary microscopic examination.

Specific Gravity.—The importance of specific gravity in concentration makes it evident that an accurate knowledge of the minerals present is necessary. The specific gravity may then be obtained by reference to a mineralogy text. Detailed examples of the application need not be cited.

Complex Minerals.—Minerals containing more than one metal of value are not uncommon. Perhaps the most important is argentiferous galena. Silver is known to occur as a solid solution in galena³ and as minute inclusions of argentite, ruby silver,

¹ COGHILL, W. H., and J. P. BONARDI, "Approximate Quantitative Microscopy of Pulverized Ores," *U. S. Bur. Mines, Tech. Paper 211*, 17 pp., 1919.

² SCHWARTZ, G. M., "Chalmersite at Fierro, New Mexico," *Econ. Geol.* Vol. XVIII, pp. 270-277, 1923; "Solving Metallurgical Problems with the Reflecting Microscope," *Eng. Mining Jour.-Press*, Aug. 11, 1923.

³ NISSEN and HOYT, "On the Occurrence of Silver in Argentiferous Galena Ore," *Econ. Geol.*, Vol. X, pp. 172-179, 1915.

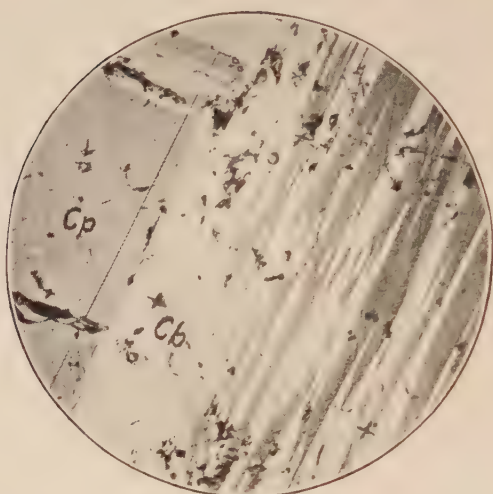


FIG. 1.—Intergrowth of chalcopyrite (Cp) and chalmersite or cubanite (Cb). The sulphides in this ore were mixed with magnetite. Magnetic separation of iron and copper was impossible as chalmersite is also magnetic. Fierro, New Mexico. $\times 75$.

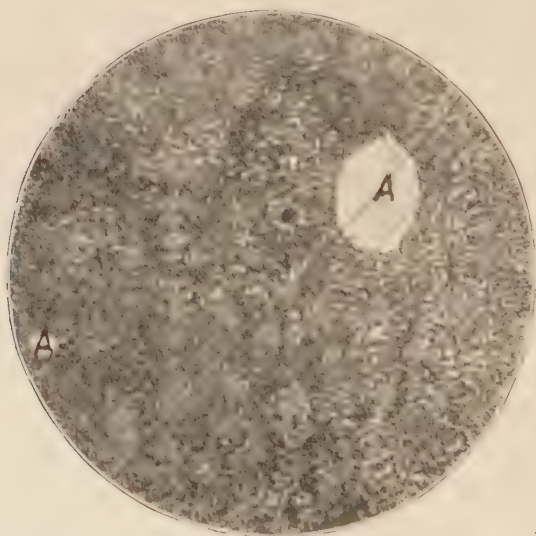


FIG. 2.—Etched surface of galena showing inclusions of argentite (A). Much of the silver of argentiferous galena is carried in this manner. Chief Consolidated mine, Eureka, Utah. $\times 140$.

tetrahedrite, and, probably, as other silver minerals (see Fig. 2). Ellis¹ has recently described the solution of a problem in the concentration of Coeur d'Alène ores where the ratio of silver to lead varied in tailing and concentrate from that in the feed. It was found that a considerable proportion of the silver occurred as minute inclusions of tetrahedrite in galena. This content would naturally follow the galena in concentration. An examination of the middling products showed, in addition, larger grains of argentiferous tetrahedrite which had been freed during grinding and, because of a lower specific gravity than galena, had tended to appear in the middling and even in the tailing. It was concluded that the system of ore dressing should include fine grinding and possibly flotation of both middling and tailing.

b. Valueless Metallic Minerals.—Valueless metallic minerals, especially pyrite and pyrrhotite, occur in many ores. Their recognition is, of course, of prime importance. Microscopic examination of polished surfaces would readily reveal these minerals and their approximate amount, thus suggesting a means of excluding them.

Singewald's early paper² gives a complete analysis of a problem of a valueless mineral intimately associated with an ore mineral. Titaniferous magnetites are not uncommon in deposits of considerable size but have not been of value because of the titanium content. It was clearly shown that part of the ilmenite was so intimately intergrown with the magnetite that there was no possibility of separating them mechanically (see Fig. 3). Holmes says in the preface to Singewald's work:

Crushing ores to 200-mesh would not insure a clean separation of the two minerals. Consequently the problem of utilizing titaniferous magnetite involves the application of chemical rather than physical methods. In short, the problem is not one of eliminating the titanium by milling, but of reducing the ores directly by some smelting process.

c. Gangue Minerals.—Gangue minerals present a problem somewhat similar to that of valueless metallic minerals. They may be often recognized in a hand specimen, but in some ores the gangue mineral may be entirely masked by the ore minerals. This was found to be especially true of a low-grade ore from the

¹ ELLIS, E. W., "Solving a Problem in Silver-lead Ore Concentration," *Eng. Mining Jour.-Press*, Nov. 20, 1926.

² SINGEWALD, *op. cit.*, 1913.

Cuyuna Range, in Minnesota.¹ An important lawsuit hinged on the possibility of concentrating the material to make it marketable. The methods of washing utilized in iron-ore concentration failed to give results at all satisfactory. Examination of polished surfaces of the ore showed the presence of innumerable silica grains averaging $\frac{1}{200}$ inch in diameter (see Fig. 4). This

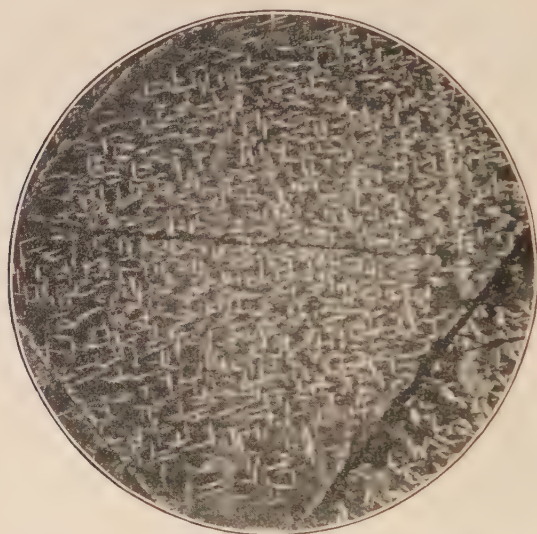


FIG. 3.—Intergrowth of ilmenite blades (white) in magnetite etched black. Minuteness of ilmenite particles precludes separation by any milling process. Ore from Duluth gabbro, Cook County, Minnesota. $\times 100$.

clearly eliminated any present commercial possibility of concentrating the material.

2. Textural Relations.—Not infrequently, the size and relation of the ore minerals are important, particularly in a complex ore on which differential flotation is to be used. The deposits at Kimberley, British Columbia, furnish illustrations of this type of ore.²

The ore of the Stewind Mine proves, on microscopic examination, to be a particularly fine-grained mixture of galena, sphalerite, and pyrrhotite. It is practically impossible to

¹ SCHWARTZ, G. M., "Solving Metallurgical Problems with the Reflecting Microscope," *Eng. Mining Jour.-Press*, Aug. 11, 1923.

² THOMSON, E., *op. cit.*, 1922. See, also, SCHWARTZ, G. M., "Microscopic Character of the Sullivan Ores," *Eng. Mining Jour.-Press*, Vol. CXXII, pp. 375-377, 1926.

crush the ore fine enough to insure a clean separation, and, thus, much costly experimentation has not proved successful. The Sullivan Mine nearby contains the same three sulphides but in a somewhat coarser mixture (Fig. 5), and selective flotation has been unusually successful.

The importance of the size of grain is emphasized in the Cuyuna hematite-silica ore described above. In another case from

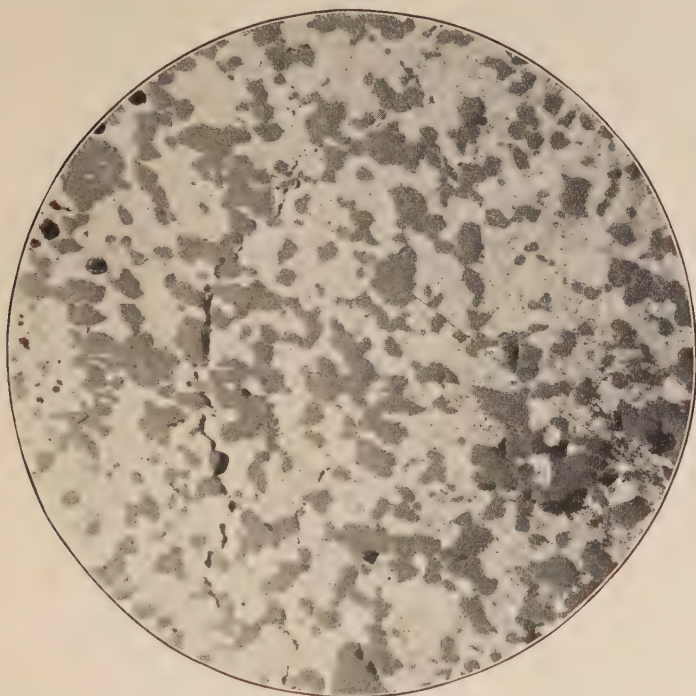


FIG. 4.—Hematite (white) with numerous minute quartz grains. A lawsuit hinged on the possibility of removing the quartz by washing. This is commercially impossible on account of the minuteness of the quartz grains. Cuyuna range, Minnesota. $\times 100$.

the same area, the problem involved the possibility of concentrating the magnetite of the magnetite slates of the Cuyuna Range according to the method used on the East Mesabi.¹ Illustrations shown by Thiel indicate that² the slate would

¹ SCHWARTZ, G. M., "New Ore of the East Mesabi," *Eng. Mining Jour.*, Vol. CXVI, pp. 409-419, 1923.

² THIEL, G. A., "Commercial Possibilities of the Magnetite Slates of the Cuyuna Range," *Eng. Mining Jour.-Press*, Nov. 8, 1924.

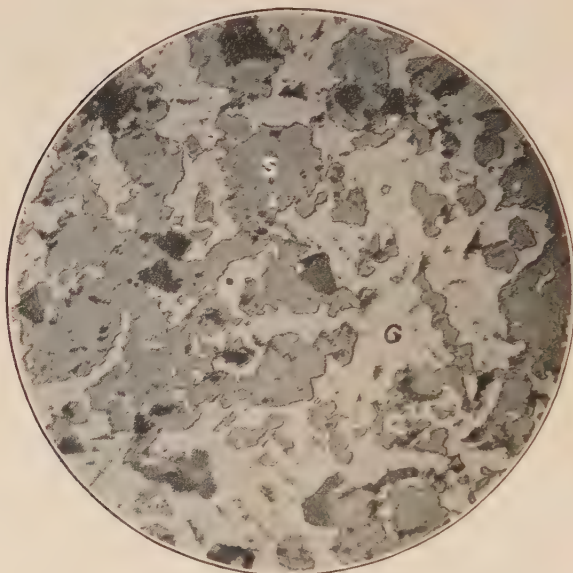


FIG. 5.—Intimate mixture of galena (G) and sphalerite (S). This is the type of ore which may be successfully treated by selective flotation. Sullivan Mine, Kimberley, British Columbia. $\times 50$.

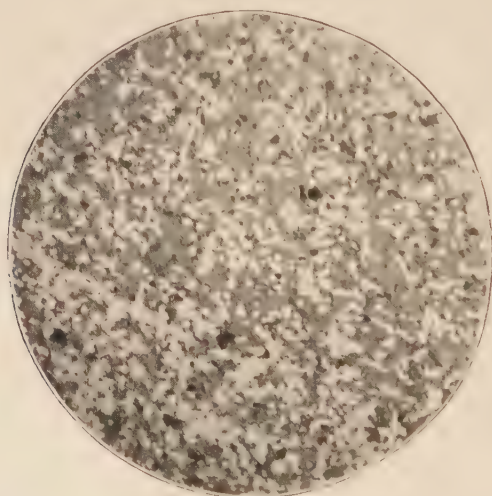


FIG. 6.—Mixture of magnetite (M) and gangue (dark). Such fine-grained material is difficult to separate. Very fine grinding and magnetic separation is fairly successful where much of material is coarser. East Mesabi range, Minnesota. $\times 70$.

require grinding to pass 200-mesh to attain even approximate separation of the magnetite and gangue. This is beyond the range of economic possibility at the present time. The texture of the ore is the determining factor.

3. Quantitative Data.—The microscope has long been used to obtain the approximate composition of rocks by carefully compiling the amounts of various minerals and then calculating the chemical composition. Somewhat similar processes may be applied to the study of ores, as has been noted by several writers. This method is extremely useful where a rapid approximate determination is needed, as the results may be obtained in a very short time, whereas a chemical analysis takes considerable time. Often it is necessary to know the amount of each mineral present, information obtainable only by microscopic examination.

By use of a binocular microscope, the grains may be counted after screening and spreading on a glass plate and then recast in terms of weight.¹ The difficulty with this method is that a mineral lightly coated by another is classified as the mineral forming the exterior. Head² describes a method of using mounted polished grains which is much to be preferred.

It is not uncommon to find in milling that the metallic content of the ore varies with the mesh to which it is crushed. If the ores are screened and the various sizes studied, the actual quantity of each mineral carrying the metal may be determined and the cause of the variations, and this, in turn, will lead to improved methods.

A very complete description and its application have been given a quantitative method where it was desired to grade up a molybdenite concentrate from a flotation mill. By determining the per cent of gangue, pyrite, molybdenite, and locked grains of silica and molybdenite in the various screen sizes, it was shown that grinding to pass 120-mesh and producing a concentrate of 75 per cent molybdenite would be most economical. Other quantitative examples are given by Thomson.³

Although each of the examples cited above has been given to show its relation to a specific point, many of the examples

¹ KIRBY, K., and F. W. APGAR, "Approximate Determination of the Minerals in Concentrates by Means of the Microscope," *Met. Chem. Eng.*, Vol. XVIII, p. 514, 1918.

COGHILL, W. H., and J. P. BONARDI, *op. cit.*

² HEAD, R. E., *op. cit.*, 1921.

³ THOMSON, E., *op. cit.*, 1922.

would serve almost equally well as illustrations of other points. As a rule, more than one of the kinds of information outlined above are of importance in a given problem. This increased knowledge of several pertinent factors, obtained by microscopic methods, is, therefore, a direct measure of the usefulness of microscopic studies.

Milling problems, as noted elsewhere, are not the only type of metallurgical problem that may be attacked by use of the microscope. Studies of slags and sinters often yield important information. The work of the metallographers on the metals and alloys is too well known to need special note.

In recent work on iron-ore sinters, the author obtained valuable information on the following points:

1. Mineral composition
 - a. Contrast with original material
 - b. Analogy of artificial to natural minerals
2. Manner of growth of crystals
3. Mode of aggregation of particles
 - a. Interlocking grains
 - b. Bond of silicates, etc.
4. Distribution of porosity

This study when completed will give an infinitely more definite and complete understanding than has existed heretofore of what actually happens in the sintering process.

At present, the author is investigating the nature of an alumina abrasive by some of the methods outlined above. Considerable variation was noted by the manufacturers in the material from different parts of an ingot. A preliminary microscopic investigation has shown that impurities, especially magnetite, remain as inclusions in the Al_2O_3 in the outer part, which cools quickly, whereas the magnetite segregates to individual grains in the interior, which cools very slowly. This factor no doubt accounts for some of the important variations in properties of abrasives from different parts of the ingot. Accurate knowledge of the variations will doubtless enable the manufacturers to make the changes necessary to produce a maximum of the most desirable abrasive.

These examples are not exhaustive but serve to illustrate the wide range of the problems whose solutions are obtainable by microscopic methods.

Conclusion.—Microscopic study preceding experiments on an ore will assist in mapping out the methods to be used. It has been shown that an accurate knowledge of the mineralogy, texture, and relative amounts of various constituents may be specifically applied to numerous problems. Moreover, this knowledge when at hand would doubtless be of value to the metallurgist in many ways other than those pertaining to magnetism, flotability, chemical composition, specific gravity, size of grain, nature of intergrowth, and quantitative relations. It is conceivable that the success or failure of enterprises may depend upon the use of microscopic data.

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